COMPILATION OF AMBIENT PARTICULATE MATTER SIZE AND COMPOSITION DATA
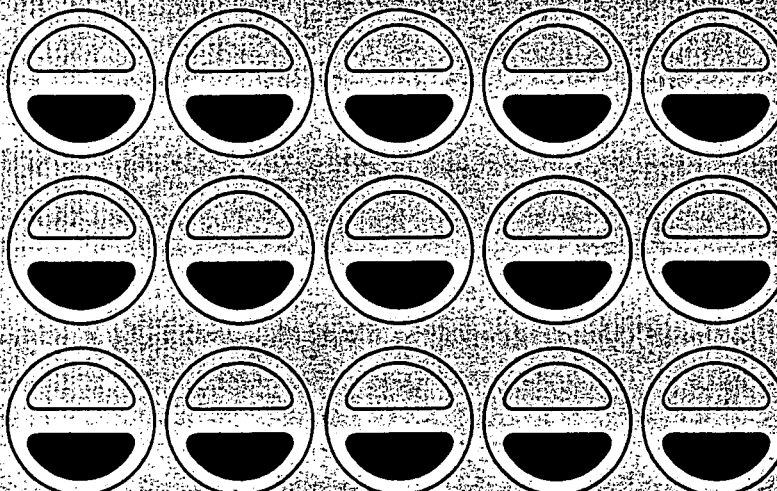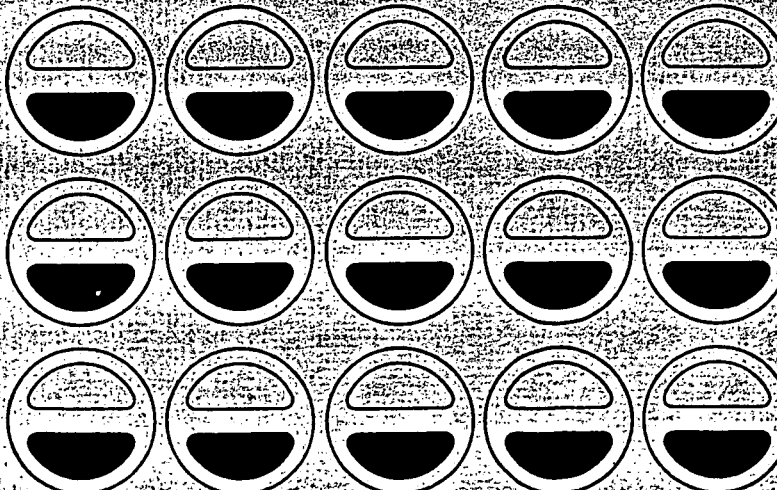
PEI ASSOCIATES

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SECTION 1.0

INTRODUCTION

1.1 BACKGROUND

Section 109(d) of the Clean Air Act as amended in 1977 requires the U.S. Environmental Protection Agency (EPA) to review the air quality criteria for the total suspended particulate (TSP) National Ambient Air Quality Standard (NAAQS) by December 31, 1980, and at 5-year intervals thereafter. As a result of these reviews, EPA shall make such revisions to the criteria and the NAAQS and shall promulgate a new NAAQS as may be appropriate in accordance with Sections 108 and 109(b) of the Clean Air Act.

The need to consider the particle size and the chemical composition of particulate matter (PM) has been a continuing concern to EPA. Since the promulgation of the TSP NAAQS in 1971, there has been considerable discussion that EPA should consider the promulgation of a size specific PM NAAQS. At the time that the current TSP NAAQS was promulgated, however, there were insufficient data to establish a size specific standard.[1]

Over the past several years, EPA has committed a substantial portion of its research effort studying the sources, effects, transport, etc., of those PM size fractions that are thought to have the greatest impacts on health and welfare.[2]

EPA is now in the process of reviewing the existing TSP NAAQS in accordance with the requirements in the Clean Air Act as amended in 1977. As part of this review, EPA has been collecting, analyzing and evaluating a wide variety of data on health and welfare effects and on emissions and ambient air quality. Some of these data have been obtained from EPA conducted studies and research; other data have been obtained from studies and research by other individuals or groups. The health and welfare effects

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data will be used by EPA to revise the criteria document and ultimately to revise the NAAQS if the revised criteria document suggests that a change in the NAAQS is appropriate. The emissions and air quality data will be used to assess the potential impacts of revising the current NAAQS.

As a result of the May 29, 1979 Federal Register "Improving Environmental Regulations: Final Report Implementing E.O. 12044", EPA is required to conduct a complete regulatory analysis of any major action it plans to take with regard to regulatory requirements. A potential revision of the TSP NAAQS constitutes a major action and therefore information on the nature and extent of the PM problem across the United States is needed to conduct such an analysis. This information should include data on the particle size and composition of the PM.

1.2 PURPOSES OF THIS STUDY

One of the purposes of this study was to provide EPA with data on PM particle size and composition (including data on the chemical and physical nature of the particulate) that could be integrated into the regulatory analysis. Another purpose of this study was to evaluate (to the extent possible) three hypotheses regarding PM. The first hypothesis is that a constant or consistent relationship exists between Inhalable Particulate (IP) and TSP. The second hypothesis is that over 50% of the fine PM mass is of anthropogenic origin. The third hypothesis is that the relationship between IP and TSP can be defined for a given geographic location, site type, chemical composition, and meteorological condition.

A third purpose of this study was to evaluate the size distribution of PM for various geographic and siting situations. The size fractions for which the data were initially summarized included particles with a mass < 1 μm, < 2.5 μm, < 10 μm, < 15 μm, 2.5 to 15 μm, and TSP as measured by the high-volume (hi-vol) air sampler which for the purposes of this study was assumed to have a median aerodynamic diameter (d_{50}) of < 30 μm.

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The fourth purpose of this study was to characterize the chemical nature of PM across the country. Typical concentration ranges of ions, carbon, trace organic substances, trace element components, and crystalline forms were to be presented. In many cases geographical, spatial or temporal factors influence the chemical characteristics of the PM and summaries were to be prepared as appropriate to determine the variations that may exist with respect to these factors. The particle size range of each chemical component was also to be presented.

The fifth purpose of this study was to characterize the typical composition of PM, according to the size ranges presented above, both in terms of the typical high and average mass concentrations for: urban, suburban or residential, remote or rural, and industrial-oriented sites.

1.3 APPROACH

On March 25-26, 1980, the Air Pollution Control Association held a specialty conference workshop on baseline data for IP. The objectives of this workshop were to identify (1) existing data on the size distributions and mass concentrations of atmospheric aerosols and (2) general features of these data applicable to characterizing size-fractionated aerosols under average and episodic conditions.[3] One of the major topics of discussion at this workshop was the use of existing air quality data to assist EPA in developing the anticipated size-specific PM NAAQS. Because these data had been collected at a number of urban and rural locations and under various meteorological conditions, there was a belief that many of the unique features represented by these data could be generalized through selective analyses. It was suggested that as a result of the workshop some conclusions could be drawn with respect to the size and the chemical composition of the PM throughout the United States. To that end, a series of studies were compiled by Dr. Paul Lioy of the Institute of Environmental Medicine, New York University Medical Center; Dr. John

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Watson of Environmental Research and Technology; and Dr. John Spengler of Harvard University School of Public Health to define the existing data base upon which selective analyses could be conducted to supplement the body of data currently being collected by EPA to support and assess the potential impacts of revising the current TSP NAAQS. The above individuals recommended that EPA examine the existing data and use these data, to the extent possible, to not only evaluate the size and chemical composition of PM across the county but also to address the hypotheses presented in Section 1.2.

In this report Section 2.0 presents the general methodology and the data base used in PEDCo's analysis. Section 3.0 discusses the theory and background on PM particle size as well as the geographic and land-use distributions of the particle size data. Section 4.0 discusses PM chemical characteristics; includes a list of elements (or components) for which information is available and the typical concentration ranges for each major element; and discusses the variability of these concentrations with geographic area. Section 5.0 presents the results of the analyses and the conclusions drawn from the analyses of existing data.

SECTION 2.0

METHODOLOGY AND DATA BASE

This section discusses the methodology or approach, the data used in the analyses identified in the methodology, and the limitations of the data base for the individual analyses.

2.1 METHODOLOGY FOR CONDUCTING THE ASSESSMENT

The first step in this study was to conduct a literature search to compose a comprehensive list of PM studies (or reports) that have been conducted over the past 5 years. This list was compared to the list of studies and references identified by Doctors Lioy, Watson and Spengler[3] (Appendix A) to identify any additional studies which should be considered for possible investigation. Abstracts of these additional studies were reviewed and specific criteria were developed to determine which studies should be included. The criteria used in this determination are listed below:

- o   Was the study conducted in an area not covered by the initial list of studies?

- o   Did the study use unique analytical techniques or measurement methods other than those used in the initial list of studies?

- o   Was the study a long-term rather than a short-term assessment?

- o   Did the study address spatial or temporal factors not considered in the initial list of studies?

Studies that met one or more of the above criteria were listed and included in the compilation.

The second step was to review each study selected in step one and summarize available information on particle size and/or

chemical or physical composition. Two summary forms (Appendix B) were developed which aided in this initial review and summarization. In addition to the basic data on particle size and the composition of the PM, other important information was also obtained during the review of these studies. The specific data that were summarized are presented in Section 2.3.

The third step was to review each study with respect to the type of data compiled to determine which data should be included in the analysis. One consideration was the sampling method. That is, was the data obtained by using a standard or reference technique? In some studies the measurement technique used may have had some inherent problems or bias. In other studies the measurement technique may only have had limited applications and therefore the reliability of the technique has not been established. Another consideration was the length of the study and the number of samples collected. Care was taken to note studies with sampling periods of less than 1 year. In those cases, these data would have certain seasonal biases that must be considered. Also noted were studies with data collected over less than 24 h. The final considerations were the area for which the study was conducted and the number of sites included in each study area. Each study identified for possible inclusion in the analysis was reviewed with respect to the above considerations, and a final list of studies was composed for analysis.

The fourth step was to prepare a preliminary outline for assessing the PM mass concentration in terms of particle size distribution and in terms of the chemical characteristics. A meeting was held with the project officer and the technical advisor (Dr. Paul Lioy) to review this outline and to develop a final outline for the required analysis.

The fifth step was to review the particle size data in the final list of studies. The data were summarized for seven geographic areas across the United States, for the cities within these geographic areas, and for five site classifications or land

uses. The initial aerodynamic size fractions for the data summaries were < 1 μm, < 2.5 μm, < 10 μm, < 30 μm, 2.5 to 15 μm, and TSP as measured by the hi-vol sampler which for the purposes of this study was < 30 μm. Particle size data were compared to determine if any generalizations could be made regarding the nature of the PM problem with respect to geographical or spatial distribution. Specifically, a decision tree analysis was conducted to determine the significance of the particle size concentration variation with respect to geographic area and site classification or land use. This analysis permits both the geographic area and the site classification to be considered in a series of analyses to determine which of the factors is the most significant in terms of characterizing the nature of PM across the United States. A series of generalized size distributions for various geographic areas and site classifications were also prepared and used for the overall comparison of particle sizes.

The sixth step was to characterize the chemical composition of PM across the United States. Typical concentration ranges of ions, carbon, trace organic substances, trace elements, and crystalline forms were summarized and compared for various data analysis techniques. To the extent possible, based on the data available, an analysis was conducted to determine the extent to which geographic, spatial or temporal factors affect the overall chemical and physical nature of PM. Where a sufficient amount of data existed, these data were normalized along geographic or spatial lines to provide some additional insight into the nature of the PM problem. In addition, a summary of the particle size range for each major chemical component was also prepared.

The seventh step was to identify the typical composition of PM for three sizes: < 2.5 μm, > 2.5 μm but < 30 μm, and < 30 μm. The mean, maximum and minimum element concentrations for each size were presented. Finally, the major components of PM were summarized for each of the site classifications and geographic areas.

The eighth and final step was to review the results of all
the individual analyses of particle size and chemical composition
and to draw specific conclusions on the nature and extent of the
PM problem across the United States and on the specific hypotheses
presented in Section 1.2.

2.2 STUDIES CONSIDERED IN THE ANALYSIS

The basic list of studies used in PEDCo's analysis are those
listed in reference 3. Additional studies were included, based
on the criteria in Section 2.1. A complete list of all studies
included in the analysis is presented in Table 1. Table 1 in-
cludes the author(s) of study; the name of the study; the reference
identification used throughout the analysis; the purpose of the
study; and the cities or areas included in the study.

2.3 TYPE OF INFORMATION COMPILED

Each of the studies contained a variety of information or
data. Some studies dealt only with collecting data on particle
size or chemical composition; others contained both. In some
studies a full range of particle size data was available; in
others only one or two size ranges were identified. Since the
purpose was to analyze the nature and extent of PM across the
United States, several pieces of information were essential.

The first piece of information summarized was the geographic
location of the study area. For the purpose of this analysis,
the United States was divided into seven geographic areas:
Northwest (NW), West Coast (W), Southwest (SW), Great Plains (GP),
Midwest (MW), Southeast (SE), and Northeast (NE). Figure 1 is a
map indicating which States were included in each geographic area.

The second and third pieces of information were the number
of sites and the site classification. For this analysis each
site was classified according to eight land use/site types:
urban (U) - industrial (Ind), urban-commercial (Comm), urban-
residential (Res), suburban (Sub) - industrial, suburban-commercial,

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TABLE 1. STUDIES REVIEWED IN ANALYSIS

Author	Name of study	Reference I.D.	Purpose	Cities included in the study
Cooper, J.A.	Medford Aerosol Characterization Study (MACS)	1	Identification of major aerosol sources in Medford Airshed	Medford, Oregon
Waggoner, Alan P. and R.J. Charlson	Aerosol Characteristics and Visibility	2	Relating aerosol properties to visibility reduction	Los Angeles, CA
Stevens, R.K., et al.	Characterization of Aerosol in the Great Smoky Mtns.	3	Six day study to measure composition of aerosol	Elkmont Campground, Tennessee
Gatz, Donald F.	Identification of Aerosol Sources in St. Louis Area Using Factor Analysis	4	Identify aerosol sources	St. Louis, Missouri
Cahill, T.A., et al.	Spatial Distribution of Primary Automobile Pollutants at Lake Tahoe	5	Analyze air quality in Lake Tahoe	Lake Tahoe, Monterey, Sacramento Bay Area, Los Angeles
Barone, J., et al.	A Multivariate Statistical Analysis of Visibility Degradation at Four California Cities	6	Multiple regression was used to interpret relationship between visibility reduction, pollutants, and meteorological conditions	Los Alamitos, Los Angeles, Oakland, Bakersfield

(continued)

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TABLE 1 (continued)

Author	Name of study	Reference I.D.	Purpose	Cities included in the study
Cahill, T.A., et al.	The Composition Size Distribution for Aerosols	7	Study designed to ascertain whether recent analysis could allow continuous monitoring of PM by size and elemental composition	Sacramento, Richmond, Livermore, Oakland, San Jose, Salinas, Bakersfield, Los Alamitos, Los Angeles, Azusa, Riverside, Indio, El Cajun
Pitchford, et al.	Regional Analysis of Factors Affecting Visual Air Quality	8	Hypothetical causes of visibility reduction are verified	Canyonlands, Bryce Canyon, Grand Canyon, Chaco Canyon, Carlsbad Cavern
Trijonis, John, et al.	Analysis of the St. Louis RAMS Ambient Particle Data	9	A variety of data analysis methods are used to study the 1976 particulate data from RAMS	St. Louis, Missouri
Kolak, N.P., J. Hyde, and R. Forrester	Particulate Source Contributions in the Niagra Frontier	10	Attempt to investigate nature of particulate composition in a heavy industrial region	Buffalo, Lackawanna, and Angola, New York
Lioy, P.J., J.G., Watson, and J.D. Spengler,	APCA Specialty Conference Workshop on Baseline Data for Inhalable Particulate Matter	11	Identified existing data on size distribution and mass concentration of aerosol and also the general features of this data	NA
Kneip, T.J., et al.	Trace Organic Compounds in the New York City Atmosphere	12	Increase knowledge of the kinds and concentrations of organic compounds in New York City air, especially those which are biologically active	New York City and Tuxedo, New York

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(continued)

TABLE 1 (continued)

Author	Name of study	Reference I.D.	Purpose	Cities included in the study
Pierson, W.R., et al.	Ambient Sulfate Measurements on Allegheny Mountain and the Question of Atmospheric Sulfate in the Northeastern U.S.	13	Contribute to understanding of visibility degradation and acid rainfall	Allegheny Mountain, Pennsylvania
Eisenbud, M. and T.J. Kneip	Trace Metals in Urban Aerosols	14	Ascertain the extent to which trace elements present in suspended dust are absorbed by New York City residents	New York City
Mueller, P.K. and G.H. Hidy	Implementation and and Coordination of the Sulfate Regional Experiment (SURE) and Related Research Programs	15	Define the relationship between emitted primary pollutants and regional ambient concentrations of secondary products	Eastern U.S. from Illinois to Maine
Watson, John	Chemical Element Balance Receptor Model Methodology for Assessing the Sources of Fine and Total Suspended Particulate in Portland, Oregon	16	Develop concept of, evaluate, and apply the chemical element balance receptor model	Portland, Oregon

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(continued)

TABLE 1 (continued)

Author	Name of study	Reference I.D.	Purpose	Cities included in the study
Lyons, C.E. and I. Tomback	Relating Particulate Matter Sources and Impacts in the Willamette Valley During Field and Slash Burning	17	Study the impact of various open burning practices on air quality	Willamette County, Oregon
Heisler, S.L., R.C. Henry and J.G. Watson	The Sources of the Denver Haze in November and December of 1978	18	Determine contribution of chemical species and emission sources to atmospheric light extinction during Denver Haze Study	Denver, Colorado
Hidy, G.M., P.K. Mueller, D. Grosjean, B.R. Appel, and J.J. Wesolowski	The Character and Origins of Smog Aerosols	19	Description of the physical and chemical nature of smog aerosols and their relationship to visibility reduction	California Air Basins
Moyers, J.L., et al.	Evaluation of Particulate Trace Species in Southwest Desert Atmosphere	20	Study distribution and composition of aerosol in arid west	Tuscon, Arizona
Camp, D.C., A.L. Van Lehn, and B. Loo	Intercomparison of Samplers Used in the Determination of Aerosol Composition	21	Evaluation of Particulate Aerosol Samplers	Charleston, West Virginia

(continued)

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TABLE 1 (continued)

Author	Name of study	Reference I.D.	Purpose	Cities included in the study
Air Quality Bureau, Montana Dept. of Health and Environmental Sciences	Montana Air Pollution Study	22	Air pollution health effects	Anoconda, Billings, Butte, Great Falls, and Missoula, Montana
Ferris, B.G., F. Spiezer, J.D. Spengler, et al.	Effects of Sulfur Oxides and Respirable Particles on Human Health	23	Population Exposure and and Health effects of SO_2 and PM	Watertown, Massachusetts, Kingston-Harriman, Tennessee, St. Louis, Missouri, Steubenville, Ohio, Portage, Wisconsin, Topeka, Kansas
U.S. EPA	Health Consequences of Sulfur Oxides: A Report from Chess, 1970-1971	24	Epidemiological studies to provide dose-response information	Los Angeles, California, Salt Lake City, Utah, St. Louis, Missouri, New York, New York, Chattanooga, Tennessee, Birmingham, Alabama, Charlotte, North Carolina, and Chicago, Illinois
Leslie, A.C.D., et al.	Aerosol Characterization for Sulfur Oxide Health Effects Assessment	25	Examine geographic trends of sulfur in fine particle mode	Pensacola and Miami, Florida

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(continued)

TABLE 1 (continued)

Author	Name of study	Reference I.D.	Purpose	Cities included in the study
Lewis, C.W. and E.S. Macias	Composition of Size-Fractionated Aerosol in Charleston, West Virginia	26	Sampling Study at a Single Site	Charleston, West Virginia
Kowalezyk, G.S., C.E. Choquette and G.E. Gordon	Chemical Element Balance and Identification of Air Pollution Sources in Washington, D.C.	27	Re-examined chemical-element balance method and applied it to samples collected in Washington, D.C.	Washington, D.C.
Lee, Robert E. and Stephen Goranson	Cascade Impactor Network	28	Size distribution of Urban Aerosol	Chicago, Cincinnati, Denver, Philadelphia, St. Louis, Washington, D.C.
Rodes, Charles E.	Protocol for Establishment of a Nationwide Inhalable Particulate Network	29	Establish magnitude of IP fraction of TSP at selected sites across the U.S.	Birmingham, Alabama, Akron/Cleveland, Ohio, Philadelphia, Pennsylvania, Los Angeles, California, Durham, North Carolina (pilot study)
Miller, F.E., et al.	Size Considerations for Establishing a Standard for Inhalable Particles	30	Present data and information on establishing a size specific particulate matter standard	

(continued)

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TABLE 1 (continued)

Author	Name of study	Reference I.D.	Purpose	Cities included in the study
Pace, T.G. and E.L. Meyer	Preliminary Characterization of Inhalable Particulate in Urban Areas	31	Provide information to those concerned with the control of particulate matter	St. Louis, Boston, Buffalo, and Philadelphia
Countess, R.J., et al.	The Denver Winter Aerosol: A Comprehensive Chemical Characterization	32	Characterize aerosol in Denver during winter season	Denver, Colorado
Cooper, J.A.	Review of a Workshop on X-Ray Fluorescence Analysis of Aerosol	33	Define the boundary conditions within which XRF can produce reliable information, define future innovations	
Bridgeman, H.A.	Measured and Theoretical Particle Size Distribution over Industrial and Rural Locations of Milwaukee: April 1976	34	Determine the variation in particle size for Milwaukee, Wisconsin	Milwaukee, Wisconsin
Cooper, J.A., and John G. Watson	Portland Aerosol Characterization Study	35	Identify major aerosol source types and quantify their contribution	Portland, Oregon
Alpert, D.J., and P.K. Hopke	A Quantitative Determination of Sources in the Boston Urban Aerosol	36	Determine composition and sources of urban particulate matter	Boston, Massachusetts

(continued)

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TABLE 1 (continued)

Author	Name of study	Reference I.D.	Purpose	Cities included in the study
Gladney, E.S., W.H. Zoller, A.G. Jones, and G.E. Gordon	Composition and Size Distribution of Atmospheric Particulate Matter in Boston Area	37	Identify sources of particulate	Boston, Mass.
Nifong, G.D., E.A. Boetther, and J.W. Winchester	Particle Size Distributions of Trace Elements in Pollution Aerosols	38	Study source processes, atmospheric transformation in heavily polluted community	East Chicago Gary, Indiana
Whitby, K.T., R.B. Husar, and B.Y.H. Liu	The Aerosol Size Distribution of Los Angeles Smog	39	Present general properties of smog size distributions	Los Angeles, California
Leaderer, B.P., et al.	Summary of the New York Summer Aerosol Study (NYSAS)	40	Characterize both chemical and physical properties upwind and in NYC in the summer	New York, N.Y.
Arnold, E. and R.G. Draftz	Identification of Sources Causing TSP Non-attainment	41	Identify nonattainment sources to develop control strategies	Decator and Quad Cities
Rahn, K.A.	Silicon and Aluminum in Atmospheric Aerosols: Crust-Air Fractionation	42	Comparison between areas	Cincinnati, Denver, St. Louis, Washington, D.C., Chicago, Philadelphia, Bayside, Tucson, San Francisco

(continued)

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TABLE 1 (continued)

Author	Name of study	Reference I.D.	Purpose	Cities included in the study
Stevens, R.K., T.G. Dzubay, G. Russwurm and D. Rickel	Sampling and Analysis of Atmospheric Sulfates and Related Species	43	Comparison of several sampling and analytical methods	New York City, Philadelphia, South Charleston, WV, St. Louis, Glendora, CA, and Portland, OR
Stevens, R.K., and T.G. Dzubay	Dichotomous Sampler - A Practical Approach to Aerosol Fractionation and Collection	44	Evaluate the operation of dichotomous sampler	St. Louis, MO
Davis, B.L.	Quantitative Analysis of Crystalline and Amorphous Airborne Particulates in the Provo-Orem vicinity, Utah	45	Determine types and quantities of discrete compounds in suspended particulate in an urban area where a combination of organics and inorganics occur together	Linden, Geneva, Provo, Utah
Courtney, W.J., et al.	Characterization of Denver Aerosol Between December 1978 and December 1979	46	Characterize the chemical and physical nature of Denver aerosol	Denver, Colorado

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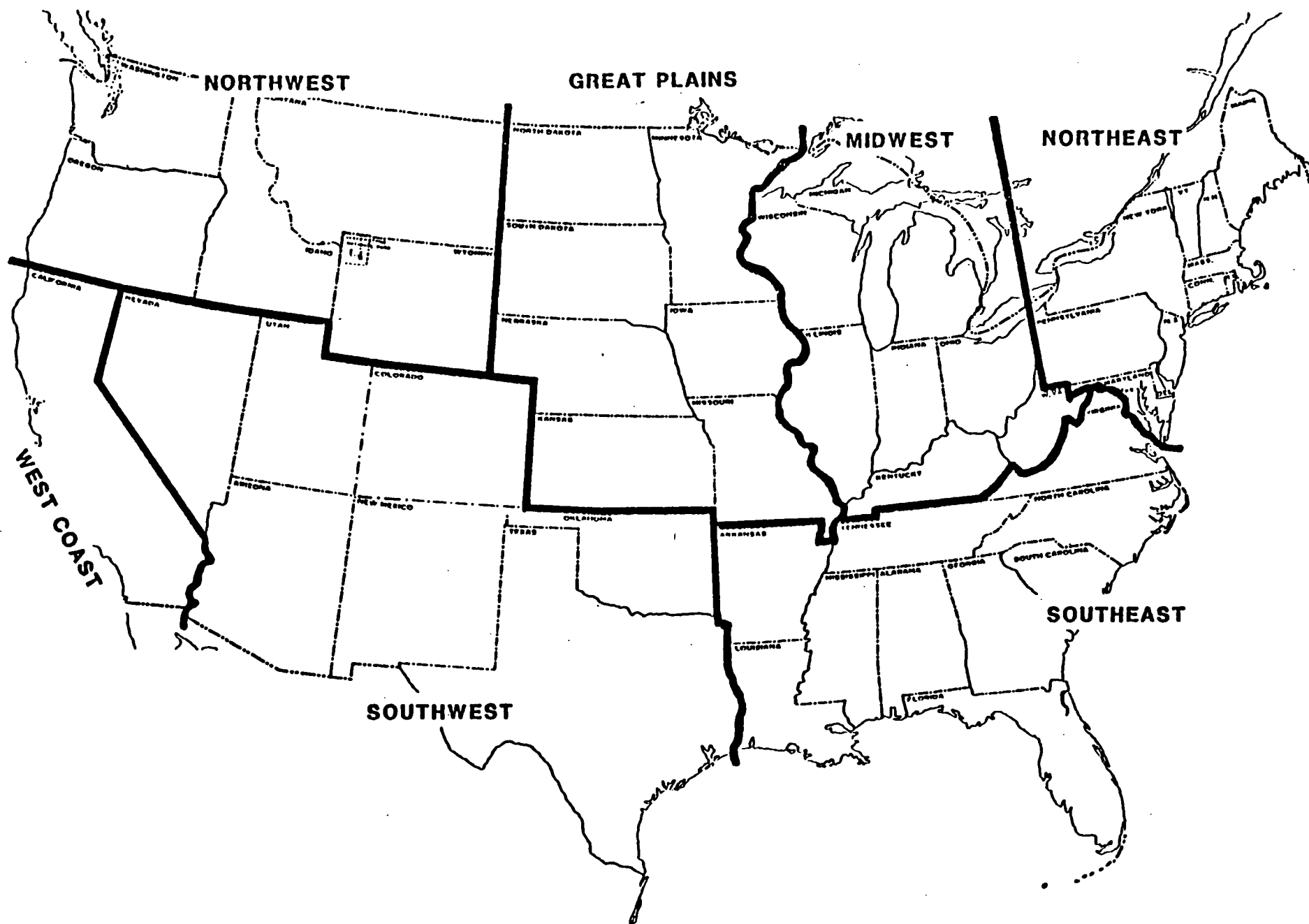
Figure 1. Geographic area classification.

suburban-residential, rural (R) - industrial, and rural-background (B).

The fourth, fifth and sixth pieces of information were the sampling period, the number of samples, and the sampling method. In most studies the sampling period was less than one year. The number of samples varied considerably. The sampling methods included the hi-vol, lo-vol, impactor, dichotomous sampler, hi-vol with cyclone, and tape sampler.

The seventh and eighth pieces of information were the particle size and the averaging time. The size fractions reported varied considerably. However, in most cases information was presented in terms of the concentration of particles ≤ 2.5 μm and TSP. In general, almost all studies that reported data had an averaging time of 24-h.

The ninth and tenth pieces of information were the chemical composition of the particle and the analytical method used to identify the various chemical components. The components for which information were generally available included trace elements, ions, carbon (C), sulfate ($SO_4^=$) and nitrates (NO_3^-).

The last information included any meteorlogical or emissions data that may have been collected in the studies. In most cases, only general meteorological data such as wind speed and direction were presented. The emissions data were limited to a general emission inventory for the study area.

Table 2 summarizes the information compiled for each study included in the analysis.

2.4 LIMITATIONS OF THE DATA BASE

Since most studies were conducted by different individuals or organizations and for different purposes, the types of information or data varied considerably. The greatest variations were the number of sites, the number of samples and the time period of the study. The time varied from a single day to an entire year. The number of sites varied from one to as many as 54. The number of samples varied from one to several hundred.

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TABLE 2.   INFORMATION INCLUDED IN STUDIES

Reference I.D.	Geo- graphic area[a]	Number of sites	Type site[b]	Sampling period	Sampling method	Number of samples	Particle size ranges	Averag- ing time	Analytical method	Chemical composition	Meteorological data	Emission data
1	NW	2 1 1	Urban, Rural, Ind.	April, 1979- March, 1980	Hi-vol,Sier- ra IIVI nuc- lepore SAD Lo-vol TSP	Every 6 days	TSP <30 μm respirable <15 μm	24-h	-	-	-	Total and FP by element
2	W	NA	NA	NA	NA	NA	NA	NA	NA	NA	Relative humidity (RH)	NA
3	S	1	Rural	Sept. 20-26, 1978	Dichotomous sampler	NS	Fine <2.5 μm Coarse <15 μm	24-h	Gas chroma- tography	-	-	-
4	GP	12	NS	1973-1975 (summer only)	Impactor	20-61	Values not reported	NS	Ion excited x-ray fluor- escence (XRF)	10-20 elements	Local	NS
5	SW W	8	NS	Six weeks 77, 4 weeks in 78	Two-stage stacked filter unit sampler	NS	Values not reported	-	Particle in- duced x-ray emission (PIXE)	Pb and S only	-	-
		6		Jan. 77 - Aug. 77				12-h				
		7		Aug. 77				12-h				
6	W	8	NS	July-Sept. 1973	Impactor	NS	3 size ranges 0.1-0.65 μm, 0.65-3.6 μm, and 3.6-20 μm	24-h	PIXE	Elements between Na and Pb	Velocity (V), Temp. (T), RH, and visibility	-
7	W	13	NS	July-Sept 1973	Impactor	NS	Same as above	24-h	Ion excited XRF	16 elements	-	-

(continued)

TABLE 2 (continued)

Reference I.D.	Geo-graphic area[a]	Number of sites	Type site[b]	Sampling period	Sampling method	Number of samples	Particle size ranges	Averag-ing time	Analytical method	Chemical composition	Meteorological data	Emission data
8	W	13	Rural	Fall 1979	NS	2 ea. week	2.5-15 μm <2.5 μm	72-h	PIXE	Elements and oxides	Visibility	-
9	GP	10	Urban, Rural	Mid 1975-1977	Hi-vol, dichotomous sampler	Every third day	Fine and coarse	24-h	NS	8 trace elements	11 meteoro-logical parameters	-
10	NE	6	Urban, Rural	18 months, Jan. 1978-July 1979	Dichotomous sampler, hi-vol	550 pairs	0-4 μm 4-15 μm	24-h	XRF ion chroma-tography	12 metals and addi-tional elements	Windspeed	-
11	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
12	NE	2	Urban, rural	Aug. 1976, Feb. 1977 and Aug. 1977	Hi-vol, aerotec-2 cyclone	NS	0-2.5 μm 0-3.5 μm	24-h 12-h	Solvent extractions	Organics	Local	-
13	NE	1	Rural	July 24, 1977 - Aug. 11, 1977	Hi-vol, impactor	35	Values not reported	12-h	Ion chromatog-raphy, XRF, neutron acti-vation	20-30 ele-ments and oxides	Local visi-bility	-
14	NE	5	Urban, Rural	1972-1974	Hi-vol, hi-vol with cyclone	Weekly	<3.5 μm	24-h	Extractions	Trace ele-ments	Local	-
15	NE MW	54	NS	1977-1979 9 sites-15 mos 45 sites one mo out of 4 sea-sons in a yr.	Hi-vol	-	<2.5, <12, <30 μm	24-h 3-h	Ion chromatog-raphy, XRF, electron spec-troscopy, flame photom-etry	Trace ele-ments, carbon, ions	Existing NWS data	-

(continued)

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TABLE 2 (continued)

Reference I.D.	Geo-graphic area[a]	Number of sites	Type site[b]	Sampling period	Sampling method	Number of samples	Particle size ranges	Averag-ing time	Analytical method	Chemical composition	Meteorological data	Emission data
16	NW	6	Urban, Ind., Res., Rural	July 1977-April 1978	LO-vol, hi-vol	NS	<30, <15, <2.5 μm	24-h, 8-h	XRF, neutron activation, ion chroma-tography	Trace ele-ments, ions and carbon	Local	Source sampling informa-tion
17	NW	11	Urban, Rural	May-Nov. 1978	Hi-vol, lo-vol, stacked filter unit, virtual im-pactor	NS	<30, <15, 2.5-15 μm	24-h	PIXE	Trace ele-ments, ions carbon	Wind data	Limited source descrip-tion
18	SW	NS	NS	Nov.-Dec. 1978	Hi-vol	NS	<30, <15, 2.5-15 μm	24-h, 4-h	Solvent ex-traction	Trace ele-ments, ions, carbon	Local	Emission inventory
19	W	Differs from analy-sis to analysis	Urban, Rural	July-Nov. 1972, July-Oct. 1973	Impactor	NS	Continuous distribution	24-h, 2-h	XRF, neutron activation, x-ray photodetec-tion spectro-scope	Trace ele-ments, ions, carbon	Complete met. data	Emission inventory
20	SW	11	Urban, Rural	1974	Hi-vol	Every sixth day	<30, <2.0 μm	24-h	Atomic absorp-tion (AA)	23 trace elements, ions	Local	-
21	MW	1	NS	May 1977	Hi-vol, cy-clone, stacked filter, dichoto-mous sampler	16 per instru-ment	<30 μm, fine, coarse	12-h	XRF, PIXE, AA, ion chromatog-raphy, beta gauge	8 trace elements, ions	Local	-

(continued)

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TABLE 2 (continued)

Reference I.D.	Geo-graphic area[a]	Number of sites	Type site[b]	Sampling period	Sampling method	Number of samples	Particle size ranges	Averag-ing time	Analytical method	Chemical composition	Meteorological data	Emission data
22	NW	34	Comm., Res.	Nov. 1977-April 1980	Hi-vol, dichotomous sampler	Every 3 days	<30, <2.5, 2.5-15 μm	24-h	NS	6 trace elements, sulfate, nitrate	Complete met.	-
23	NE, S, MW, GP	6	NS	Fall 1974-Spring 1977	Cyclone pre-sampler, others not specified	Every 3 days, every 6 days, selected days	<3.5, <30, <2.5; 25-15 μm	24-h	AA, neutron activation, electron spectroscopy	Trace elements, sulfates	-	-
24	W, SW, GP, NE, S	NS	Urban, Sub., Rural	1969-1974	Impactors, cyclones, hi-vol, AISI tape sampler	Daily, every 2-h	<30 μm	24-h, 2-h	Turbidimetric method, hydrazine sulfate-copper sulfate method	A few trace elements, sulfate nitrates	Local	Source descrip-tions
25	S	10	NS	July-Aug. and Dec. 1976	Impactor	NS	<2 μm >2 μm	24-h	NS	NS	Local	-
26	MW	1	Urban	21 days summer 1976	Dichotomous virtual im-pactor	5 samples for 21 days	<3.5 μm >3.5 μm	24-h	XRF, ion chromatography	Trace ele-ments	-	-
27	NE	4	Urban, Sub	Summer 1974	Impactor	NS	NS	24-h	Neutron acti-vation, AA	27 elements	-	Source descrip-tions

(continued)

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TABLE 2 (continued)

Reference I.D.	Geo-graphic area[a]	Number of sites	Type site[b]	Sampling period	Sampling method	Number of samples	Particle size ranges	Averaging time	Analytical method	Chemical composition	Meteorological data	Emission data
28	NE, SW, NW, GP	6	NS	1970	Impactor	125	<1, <2, <30 μm	24-h	None	-	-	-
29	NE, S, MW, W	5	Urban	1979-	Size selective hi-vol, dichotomous sampler	NS	<2.5, <15, 2.5-15, <30 μm	24-h	NS	Trace elements, sulfate, nitrate	Local	-
30	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
31	NA	NS	NS	Variable	Hi-vol, dichotomous sampler	6	Total, <15 μm	24-h	-	-	-	-
32	SW	1	-	Nov.-Dec. 1978	Hi-vol, Sierra, dichotomous, sequential filter	40	<2.5 μm >2.5 μm	4-h 12-h 24-h	Ion chromatography, spectrophotometry, XRF	Trace elements, sulfate, nitrate	-	-
33	NA	-	-	-	-	-	-	-	XRF	-	-	-
34	MW	2	Ind., Rural	6 days	Aircraft	-	.1-10 μm	24-h	-	-	-	-
35	NW	6	Urban, Ind., Res., Rural	1 yr.	Hi-vol, hi-vol + Sierra Cascade impactor, lo-vol	1300	<2 μm >2 μm	24-h	Ion chromatography, flame ionization, XRF, neutron activation	27 elements	Local	Emission inventory

(continued)

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TABLE 2 (continued)

Reference I.D.	Geo-graphic area[d]	Number of sites	Type site[b]	Sampling period	Sampling method	Number of samples	Particle size ranges	Averag-irg time	Analytical method	Chemical composition	Meteorological data	Emission data
36	NE	8	Urban	9 month	-	90	-	24-h	Neutron acti-vation	16 elements	-	-
37	NE	3	Comm., Res.	Feb.-Mar. 1970	Cascade im-pactor, 6-stage	9	.1-10 μm	24-h	Neutron acti-vation	18 elements	Local	-
38	MW	-	-	-	Anderson Cascade Impactor 7-stage	-	.1-9 μm >9 μm	-	Neutron acti-vation	29 elements	-	-
39	W	-	-	Aug.-Sept. 1969	Minn. Aero-sol analyz-ing system	363	.003 - 6.8 μm	1-h 6-h 24-h	-	-	-	-
40	NE	2	Urban, Rural	July-Aug. 1976	Hi-vol, optical particle counter, Anderson impactor	39	.1-10 μm >3.0 μm	1-h	AA, neutron activation, gas chroma-tography	Selected elements	Local	-
41	MW	7	-	Jan.-Dec. 1977	Hi-vol	63	1-100 μm	24-h	Polarized light microscopy	6 elements	Local	General inventory
42	NE, MW GP, SW, W	-	-	-	-	-	-	-	-	22 elements	-	-

(continued)

TABLE 2 (continued)

Reference I.D.	Geographic area[a]	Number of sites	Type site[b]	Sampling period	Sampling method	Number of samples	Particle size ranges	Averaging time	Analytical method	Chemical composition	Meteorological data	Emission data
43	NE, MW, GP, NW, W	-	-	-	Dichotomous Sampler	-	<3.5 μm >3.5 μm	2-h 24-h	XRF, ion chromatography,	Trace elements, sulfate	-	-
44	GP, MW	2	Urban, Rural	Aug. 18-Sept. 7, 1975	Dichotomous Sampler	-	<3.5 μm >3.5 μm	-	Ion chormatography	Sulfate	-	-
45	W W	6	NS	Oct. 1979 Jan. 1980	Hi-vol, lo-vol	8	<30 μm	860-5091 min	X-ray diffraction	Trace elements, oxides	Local	Source descriptions
46	SW	2	Comm.	Dec. 1978 Dec. 1979	Dichotomous Sampler	-	<2.5 μm 2.5-15 μm	4-h 8-h 12-h 24-h	XRF, ion chromatography	Trace elements, sulfate, nitrate	-	-

The geographic areas of the studies also varied. Figure 2 which identifies the States where data were available, shows that not all States (or areas) of the county were represented by these studies. Also, even though some data were available for an area it may be very limited in terms of its general application (i.e., only one site; one or two days worth of sampling; only a few samples were taken).

Another limitation of the data is that the data were obtained using a variety of measurement and/or analytical techniques. In many cases, the data were collected using techniques where sampling problems exist--for example, particle bounce when filters are used in impactors, effects of wind direction on certain samplers, variable particle size cutpoints.

Since very few studies were conducted for an entire year, some data have seasonal biases. On the other hand, only having data for a few quarters does permit an analysis of seasonal variability that might exist regarding particle size or chemical composition.

In addition, there was also quite a bit of variability in the particle size data. Some studies used a particle cut size of 3.5 µm, others used 2.5 µm, and still others used 4 or 5 µm. Most studies that measured a coarse fraction made a particle size cut at 15 µm, however, no studies provided data on a cut size of 10 µm.

Finally, only three of the studies provided any information on the quality assurance procedures that may have been used or the quality of the data reported in the studies. Although the other studies did not provide specific information on the quality assurance procedures, it was assumed that the data from these other studies were collected and analyzed using reasonable procedures and practices to ensure good quality data.

As noted above, there are many limitations associated with the studies compiled for this analysis. Therefore, each study and its corresponding data were carefully reviewed and evaluated before these data were included in the analyses or compilation of

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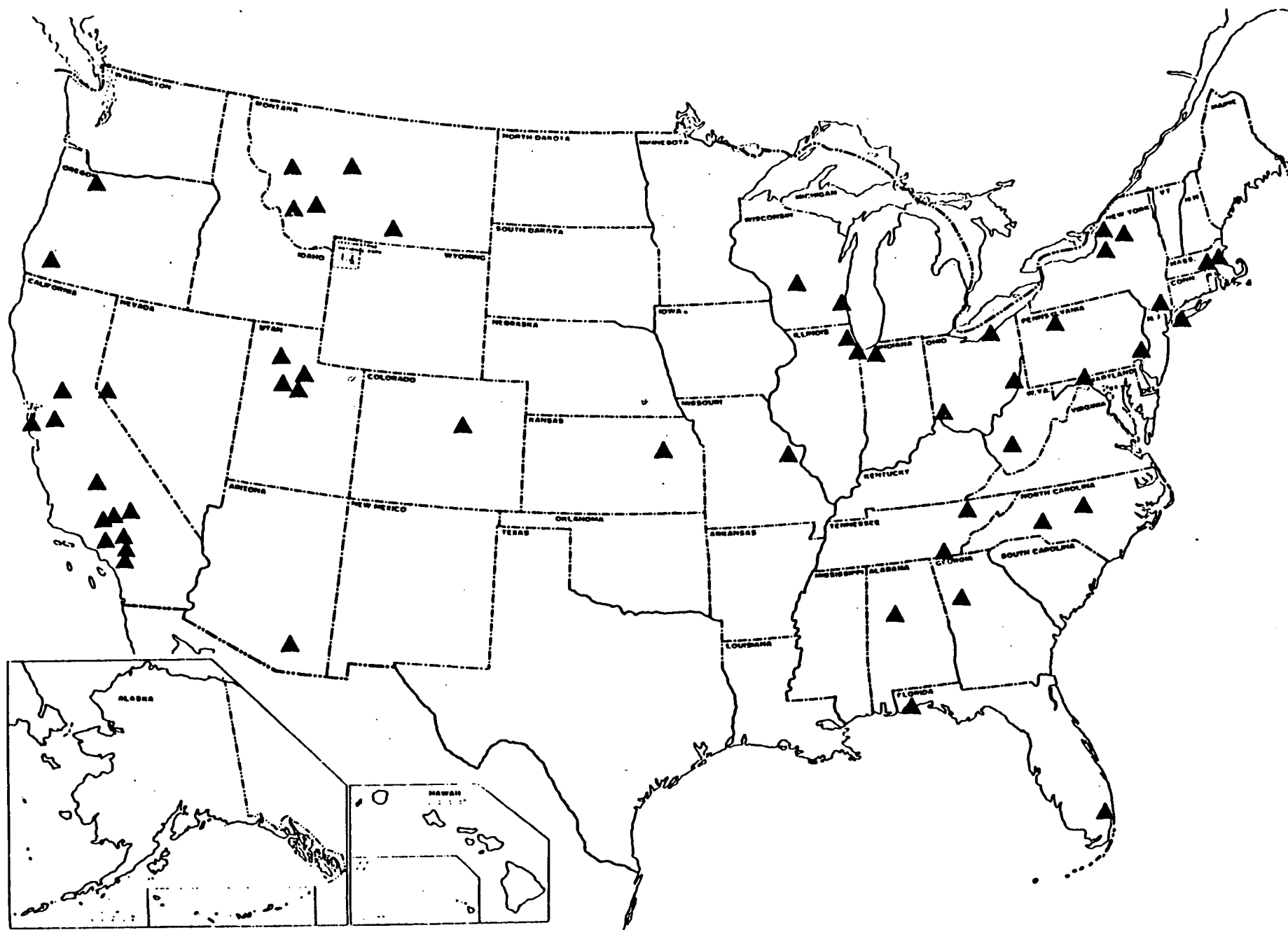
Figure 2. Areas where studies were conducted.

data in Section 3.0 and 4.0. These data were also carefully reviewed and any questions noted regarding the results and conclusions presented in Section 5.0. Even though the individual studies may have limitations, collectively these studies provide a reasonable data base from which to draw conclusions regarding the nature and extent of PM across the United States. These data also provide some valuable insight into the concentrations to be encountered if a size-specific PM NAAQS is established.

SECTION 3.0

PARTICLE SIZE DISTRIBUTION

This section discusses particle size, the results of the analyses conducted on the particle size distribution of PM across the country, and the results of a decision-tree analysis of the data from the studies.

3.1 GENERAL DISCUSSION

3.1.1 Definition of Particle Size

For the purpose of this study, an aerosol is defined as "...a complex system consisting of gas containing suspended particles. The term carries a connotation that the suspension is relatively stable."[4] Particles on the other hand "...are aggregrations of matter, either solid or liquid, larger than individual molecules. This places a lower size limit in the vicinity of 0.001 μm."[4] While this definition implies no upper size limit, generally particles larger than 100 μm are usually excluded from considera- tion because these particles fall out so rapidly that an aerosol that would contain these particles would be relatively unstable. Thus, particles or what is commonly referred to as PM applies to particles in the 0.001 μm to 100 μm range.[4]

Particle size may be defined in a number of different ways. If a solid particle is irregular in shape like the one in Figure 3,[5] it can be defined by a projected area diameter--that is, the diameter of a circle with the same area as that of the particle; the Feret's diameter, which is the maximum dimension of the particle; or the Martin's diameter, which is the length of a line segment bisecting the particle into two equal areas. While there are other ways to define a projected area of a particle, these three are the most common.[6,7]

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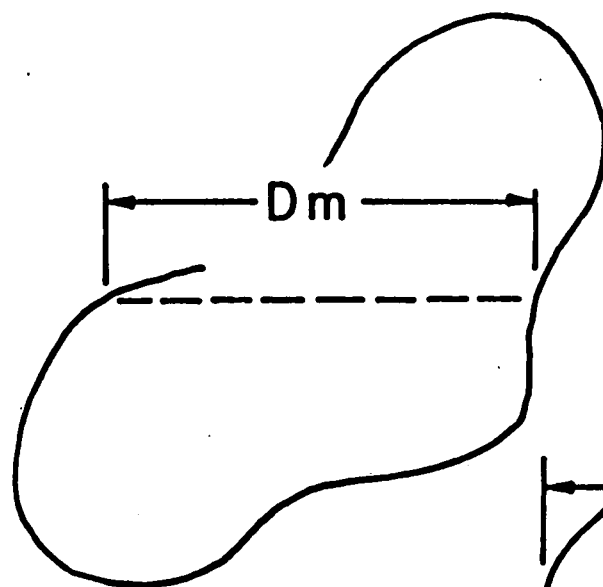
MARTIN'S DIAMETER
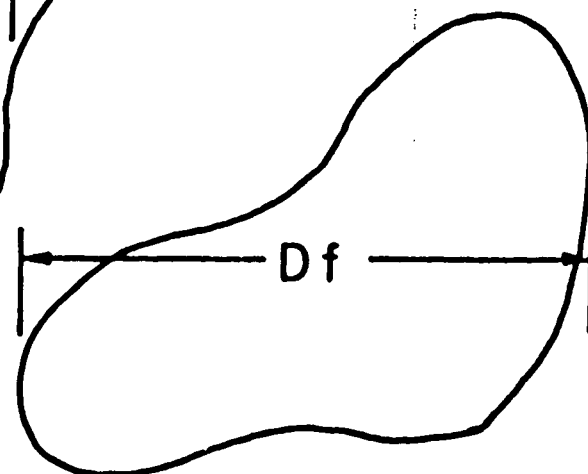
FERET'S DIAMETER
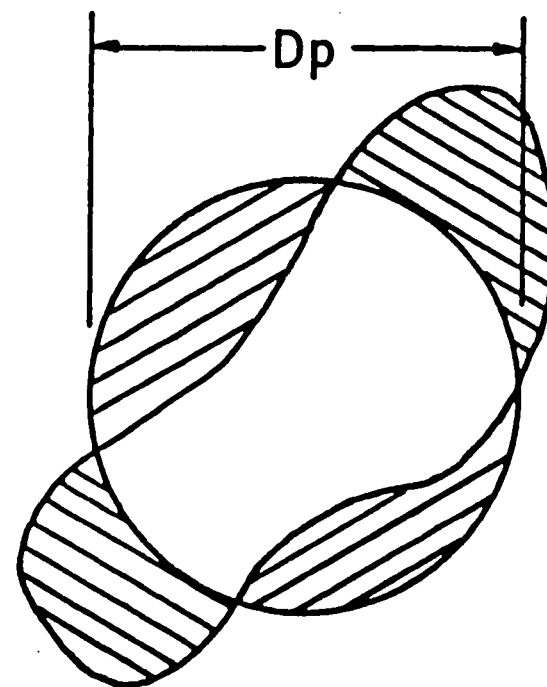
PROJECTED AREA DIAMETER

Figure 3.   Particle diameter definition for irregularly shaped particles.[5]

In addition to specifying a size of the particle by a two-dimensional projection, the size can also be defined based on its aerodynamic characteristics. The two most commonly used diameters are aerodynamic and stokes. Stokes diameter is defined "...the diameter of a hypothetical sphere having the same terminal set-tling velocity as the particle in question and having the same density as the particle material whatever its size or shape."[8] Aerodynamic diameter is "...the diameter of a hypothetical sphere of unit density having the same terminal settling velocity as the particle in question, regardless of its geometric size, shape and true density."[8] Aerodynamic diameter is probably the most fre-quently used of the two diameters to measure particle size since most of the effects (with the exception of optical) depend on the motion of the particles in air.[4]

Once the particle diameter has been chosen to specify the size of the particles, the size distribution can be plotted graphically as a frequency and/or a cumulative distribution.[6] Particle size distributions oftentimes can be approximated by a particular mathematical function. Although both normal and lognormal distribution functions have been used to represent particle size distributions, in most cases the particle size distribution is skewed and the data can be approximated by a lognormal distribution. To demonstrate the appearance of a lognormal distribution, the number, surface area and volume distributions have been plotted on a lognormal probability graph, as shown in Figure 4. Lognormal distributions are usually char-acterized by two parameters: the geometric mean and the geo-metric standard deviation. The geometric mean can be found graphically as the particle size at the 50% probability. One standard deviation from the geometric mean is the 15.9% or the 84.1% value on the probability scale. In addition to number, area, and volume distribution, the weight distribution of the particle size is also important. In the weight distribution, the 50% value indicates that half of the total mass is represented by particles whose diameters are greater than the given diameter and
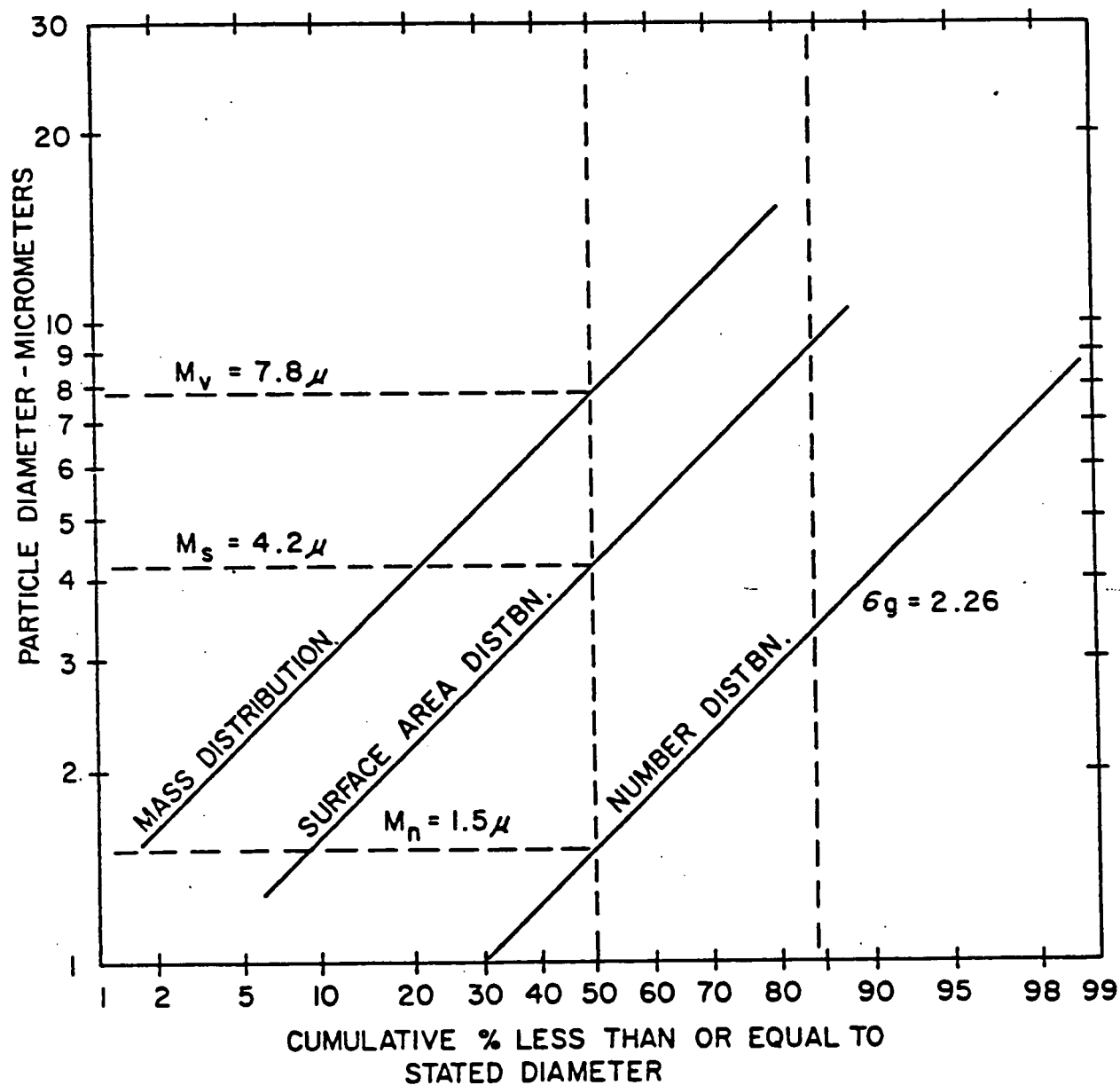
Figure 4. Log-probability plots of number, surface, and mass particle size distributions.[5]

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half are represented by particles having diameters less than the given diameter. This diameter is referred to as the mass median diameter and is abbreviated as D_{50}.[8]

3.1.2 Distribution of PM in the Atmosphere

Data collected during the 1970's indicated the existence in the ambient air of three separate modes of particles having essentially independent behavior and existence from each other.[9] The first of these modes, often referred to as nuclei mode, is below 0.1 μm and generally consists of primary particles emitted as a result of fuel combustion. The particles in this size range are formed by condensation from the gaseous phase and only exist for a very short time due to coagulation. A second mode lies in the range of 0.1 μm to about 2 μm. These particles can have a typical airborne lifetime on the order of several days. This mode is the accumulation mode and the particles are commonly referred to as fine particles. These particles are largely formed by coagulation of particles from the smaller mode and by condensation of additional particles on previously coagulated particles. The third and final mode lies in the particle size range above about 2 μm. This mode generally contains particles that are produced by mechanical processes. These particles can be removed by both rainout and sedimentation and as a result may only tend to exist in the atmosphere for a few hours. This mode is often referred to as the coarse mode. Although these larger size particles are not very numerous, they can constitute as much as 90% of the TSP atmosphere especially in dry windy climates.[4] Figure 5 shows this trimodal particle size distribution.[19]

3.2 GEOGRAPHIC DISTRIBUTION

Table 3 summarizes the particle size data by seven geographic areas: Northwest, (NW), West Coast, (W), Southwest, (SW), Great Plains, (GP), Midwest, (MW), Northeast, (NE), and Southeast, (SE). No particle size data were available for particles ≤ 2.5 or ≤ 15 μm for any W sites. Although the California Air Resources

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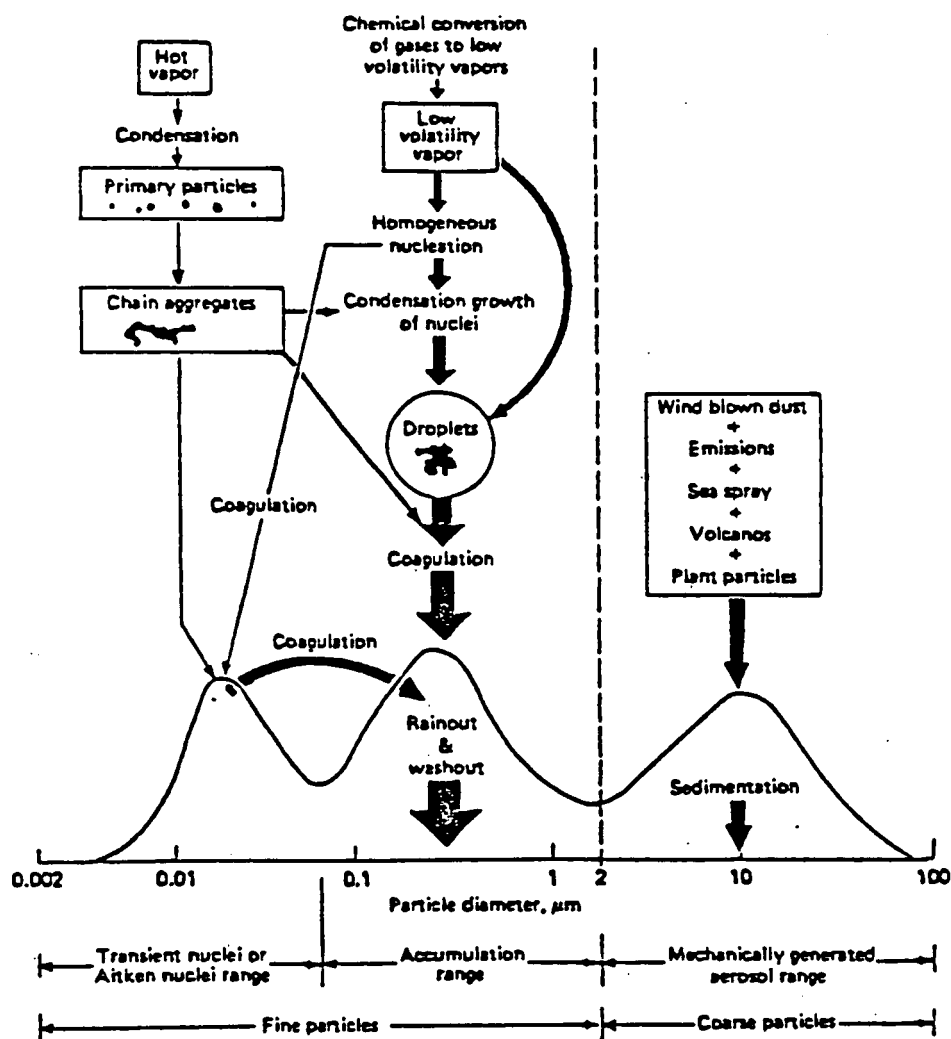
Figure 5.   Theoretical schematic of an atmospheric aerosol
surface area/mass distribution.[19]

TABLE 3. PARTICLE SIZE BY GEOGRAPHIC AREA

Area	$D_5 \leq 2.5$ μm			$D_{50} \leq 15$ μm			$D_{50} \leq 30$ μm		
	Min.	Max.	Mean (SD)[a]	Min.	Max.	Mean (SD)[a]	Min.	Max.	Mean (SD)[a]
NW	10.5	29.2	21.6 (6.5)	14.7	57.9	37.2 (12.2)	27.2	185.1	75.3 (32.5)
W[b]	-	-	-	-	-	-	180	262	200.3 (48.5)
SW[c]	21.0	21.0	-	43.0	43.0	-	59.7	104.4	83.5 (46.0)
GP	16.0	28.0	20.7 (3.7)	31.0	57.0	41.5 (8.7)	53.0	99.0	71.4 (15.1)
MW	33.1	55.0	40.5 (12.6)	-	-	-	74.3	104.0	90.5 (13.0)
SE[c]	24.0	24.0	-	56.0	56.0	-	-	-	-
NE	31.4	103.1	66.3 (35.9)	15.9	92.0	55.9 (22.9)	25.5	105.8	74.2 (26.4)
All areas	10.5	103.1	26.14 (16.1)	15.9	92.0	44.42 (15.0)	25.5	262	81.75 (39.9)

[a]Standard deviation.

[b]Only two sites with data <30 μm and no sites with data <2.5 or <15 μm.

[c]Only one site with data <2.5 or <15 μm.

Board had funded a study by the air quality group at the Crocker Nuclear Laboratory to collect particle size data at a number of sites throughout California, the cut sizes on the impactors used in this study were not comparable with those used in this analysis. Since only three discreet cut sizes were used in the California study: 0.1 to 0.65 μm; 0.65 to 3.6 μm; and 3.6 to 20 μm, and a continuous particle size distribution was not available, these data could not be used in the analysis.

Table 3 indicates that for particles $\leq$ 2.5 μm and $\leq$ 15 μm the highest maximum concentrations are in the NE and the lowest minimum concentrations are in the NW and the GP. For particles $\leq$ 2.5 μm, the concentrations range from 10.5 to 103.1 μg/m³, with the highest maximum concentration in the NE and the lowest minimum in the NW. For particles $\leq$ 15 μm, the concentrations range from 14.7 to 92 μg/m³ again with the highest maximum concentrations in the NE and the lowest minimum in the NW. However, for particles $\leq$ 30 μm, the lowest minimum concentration for particles $\leq$ 30 μm is 25.5 μg/m³ which is recorded in the NE and the highest and second highest maximum concentrations (262 and 185.1 μg/m³) were recorded in the W and NW respectively. It should be noted that in some cases the concentration for particles $\leq$ 2.5 μm is higher than the concentration for particles $\leq$ 15 μm. The major reason is that the same sampling device was not used in all cases to sample both particle sizes. Because the data in many cases were limited to only a few cities within a geographic area (even in areas like the NE), conclusions regarding a typical concentration associated with a specific particle size in a geographic area are inappropriate. However, the ratio of the average concentration for particles $\leq$ 15 μm to the average concentration for particles $\leq$ 30 μm for the entire county (0.54), is consistent but slightly lower than the ratios presented in Reference 23 for many individual monitoring sites across the county.

3.3 PARTICLE SIZE DISTRIBUTION WITH RESPECT TO SITE CLASSIFICATION OR LAND USE

Table 4 summarizes particle size data by the eight land use/ site type classifications: urban-industrial, commercial, residential; suburban-industrial, commercial, residential; and rural-industrial, background. For the studies that did not classify the sites, either the SAROAD site listing or a local map was used to determine the classification. In some cases, because very little information was available regarding the site, the site classification had to be assumed based on the best information available.

Table 4 indicates that the highest maximum concentration for particles $\leq$ 2.5 µm is 103.1 µg/m^3 at an urban-commercial site and that the lowest minimum concentration is 13.1 µg/m^3 at a rural-background site. For particles $\leq$ 2.5 µm, the highest mean concentrations, 32.7 and 32.6 µg/m^3, were at the urban-commercial and urban-industrial sites and the lowest mean concentration, 16.7 µg/m^3, was recorded at the rural-background sites. For particles $\leq$ 15 µm, the highest maximum concentration, 92.0 µg/m^3, was at an urban-industrial site and the lowest minimum, 14.7 µg/m^3, at a rural-background site. Urban-industrial sites had the highest mean concentration. For particles $\leq$ 30 µm, the lowest minimum concentration was at a rural-background site and the highest maximum concentration at a urban-industrial site. Again, the highest mean concentration was calculated for the urban-industrial sites, followed by the urban-commercial sites. It should be pointed out, however, that there were no suburban-commercial and suburban-industrial sites with particle size data $\leq$ 15 µm and no suburban-commercial sites with particle size data $\leq$ 30 µm--compared to 7 urban-industrial sites, 13 urban-commercial sites, 9 suburban-residential, and 12 rural-background sites with particle size data $\leq$ 15 µm and 10 urban-industrial, 37 urban-commercial, 12 suburban-residential, and 16 rural-background sites with particle size data $\leq$ 30 µm. One general observation should be made regarding the particle size by site classification;

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TABLE 4. PARTICLE SIZE DISTRIBUTION BY SITE CLASSIFICATION ($\mu g/m^3$)

Site classification	$D_{50} < 2.5\ \mu m$				$D_{50} < 15\ \mu m$				$D_{50} < 30\ \mu m$			
	Min	Max	Mean[1] (SD)	No. of sites	Min	Max	Mean[1] (SD)	No. of sites	Min	Max	Mean[1] (SD)	No. of sites
Urban												
Industrial	31.7	33.4	32.6 (1.2)	2	46.0	92.0	63.3 (15.7)	7	66.5	185.0[1]	97.6 (34.1)	10
Commercial	18.8	103.1	32.7 (19.5)	21	31.7	70.0	48.8 (9.7)	13	56.3	164.2	96.1 (38.9)	37
Residential	-	-	-	0	-	-	-	0	-	-	-	0
All	18.8	103.1	32.6 (18.6)	23	31.7	92.0	53.9 (13.7)	20	56.3	164.2	96.4 (37.6)	47
Suburban												
Industrial	0	0	0	0	-	-	-	0	42.6	42.6	42.6 (-)	1
Commercial	-	-	-	0	-	-	-	0	-	-	-	0
Residential	18.0	20.3	19.1 (0.9)	6	35.0	50.0	38.6 (5.1)	9	53.0	81.6	66.2 (10.3)	12
All	18.0	20.3	19.1 (0.9)	6	35.0	50.0	38.6 (5.1)	9	53.0	81.6	64.4 (11.8)	13
Rural												
Industrial	-	-	-	0	31.4	31.4	31.4 (-)	1	96.7	96.7	96.7 (-)	1
Background	13.1	24.0	16.7 (3.0)	9	14.7	56.0	32.4 (10.9)	12	25.5	68.0	45.6 (13.4)	16
All	13.1	24.0	16.7 (3.0)	9	14.7	56.0	32.3 (10.5)	13	25.3	96.7	48.6 (17.9)	17

[1]SD - standard deviation

that is, the SD associated with the means calculated for each site classification was generally lower than the corresponding SD's associated with the means calculated for each of the geographic areas.

3.4 RESULTS OF PARTICLE SIZE DISTRIBUTION ANALYSIS

Table 5 summarizes the particle size data by geographic area and site classification. The data were combined to determine if additional conclusions could be drawn after reviewing the data on the site classifications within a given geographic area. Table 5 indicates that in general, the urban-industrial sites had the highest maximum concentrations within a geographic area, followed by urban-commercial, suburban-residential, and rural-background sites for all three particle sizes ($\leq$ 2.5, $\leq$ 15 and $\leq$ 30 μm) included in the analysis. Thus, particles $\leq$ 2.5 μm and $\leq$ 15 μm generally have the same relative distribution of concentration by site classification as particles $\leq$ 30 μm.

One of the objectives or purposes of this analysis was to determine the nature and extent of the PM across the United States and to gain a better understanding of the relationship between the concentration for a particular particle size and the geographic area or site classification represented by this concentration. In order to gain this additional understanding, a powerful statistical tool--decision-tree analysis was used.

The decision-tree analysis offers several advantages over more conventional data analysis techniques (e.g., multiple linear regression). These include:[24]

o   The decision tree analysis is a nonparametric technique based on a general form of the least squares principle.

o   The decision tree analysis does not involve restrictive assumptions such as additivity and linearity.

Because the standard decision-tree programs of CART or AID were not available on any computer system for which PEDCo could gain access during the course of this study, a modified decision-tree analysis was conducted by using the statistical package in the INFORM program available from United Computing Systems, Inc.,

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TABLE 5. SUMMARY OF PARTICLE SIZE DATA BY SITE TYPE/AREA

	$D_{50} \leq 1$ μm Conc, μg/m³	$D_{50} \leq 2.5$ μm Conc, μg/m³	$D_{50} \leq 15$ μm Conc, μg/m³	$D_{50} = 2.5 - 15$ μm Conc, μg/m³	$D_{50} \leq 30$ μm Conc, μg/m³
Northwest					
U-C - Medford (1)			39.5		96.9
- Portland (16)		29.2			79.9
- Flavel Park (16)[a]		26.5			80.6
- Billings (22)[a]		18.8	44.6	26.4	79.0
- Billings (22)					73.6
- Butte (22)					90.7
- Missoula (22)[a]		27.0	57.9	33.4	100.6
- Missoula (22)					90.3
- Missoula					121.1
- Portland (35)[a]		27.1			78.6
- Portland (35)		24.0			76.5
- Portland (35)		26.7		27.6	99.4
- Portland (43)[a]		20.9			
Average		25.0	47.3	29.1	88.9
Standard Deviation		3.5	9.5	3.7	13.8
R-I - White City (1)			31.4		96.7
U-I - Portland (16)		31.7			75.5
U-I - Portland (16)		33.4			185.1
Average		32.6	31.4		119.1
Standard Deviation		1.2	-		58.1
S-R - Billings (22)					57.3
Butte (22)[a]		20.3	35.2	18.9	81.6
Butte (22)[a]		18.1	35.2	18.9	64.9
Butte (22)[a]					72.9

(continued)

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TABLE 5 (continued)

	$D_{50} \leq 1$ μm Conc, μg/m³	$D_{50} \leq 2.5$ μm Conc, μg/m³	$D_{50} \leq 15$ μm Conc, μg/m³	$D_{50} = 2.5 - 15$ μm Conc, μg/m³	$D_{50} \leq 30$ μm Conc, μg/m³
Great Falls (22)		10.5		18.2	42.6
Portland (35)		20.1			65.4
Average		17.3	35.2	18.9	65.5
Standard Deviation		4.6	0.0	0.4	14.5
R-B - Dodge Road (1)			14.7		27.2
Sauvie Island (16)		16.7			35.9
Carus (16)		16.2			32.3
Anaconda (22)[a]		15.5	39.3	23.3	52.2
Portland (35)		13.1			43.3
Portland (35)		15.5			32.3
Average		15.4	27.0	23.3	37.4
Standard Deviation		1.4	17.4	-	9.0
West Coast					
U-C - Pomona					180.0
- Rubidoux					262.0
Southwest					
U-C - Tuscon (20)					111.0
- Denver (28)					59.7
- Denver (32)		21.0	43.0		104.4
- Lindon (45)					164.2
- BYU (45)					49.4
Average		21.0	43.0		97.7
Standard Deviation		-	-		45.9

(continued)

TABLE 5 (continued)

	$D_{50} \leq 1$ μm Conc, μg/m³	$D_{50} \leq 2.5$ μm Conc, μg/m³	$D_{50} \leq 15$ μm Conc, μg/m³	$D_{50} = 2.5 - 15$ μm Conc, μg/m³	$D_{50} \leq 30$ μm Conc, μg/m³
U-I - Geneva (45)					66.5
Average					66.5
Standard Deviation					-
R-B - Tuscon (20)					29.1
Average					29.1
Standard Deviation					-
Great Plains					
U-C - St. Louis (9)		24.0	49.0	25.0	84.0
- St. Louis (9)		28.0	60.0	32.0	96.0
- St. Louis (9)		23.0	46.0	23.0	88.0
- St. Louis (9)		24.0	48.0	25.0	77.0
- St. Louis (9)		24.0	48.0	24.0	80.0
- St. Louis (9)		21.0	44.0	23.0	79.0
- St. Louis (28)					73.1
Average		24.0	49.2	25.3	82.4
Standard Deviation		2.3	5.6	3.4	7.7
U-I - St. Louis (31)			57.0		99.0
- St. Louis (31)			46.0		90.0
- St. Louis (31)			49.0		91.0
Average			50.7		93.3
Standard Deviation			5.7		4.9
S-Res. - St. Louis (9)		19.0	37.0	15.0	54.0
- St. Louis (9)		19.0	38.0	19.0	60.0

(continued)

TABLE 5 (continued)

	$D_{50} \leq 1$ µm Conc, µg/m^3	$D_{50} \leq 2.5$ µm Conc, µg/m^3	$D_{50} \leq 15$ µm Conc, µg/m^3	$D_{50} = 2.5 - 15$ µm Conc, µg/m^3	$D_{50} \leq 30$ µm Conc, µg/m^3
S-Res. - St. Louis (9)		18.0	35.0	17.0	66.0
- St. Louis (9)		20.0	37.0	17.0	53.0
- St. Louis (31)			44.0		80.0
- St. Louis (31)			36.0		54.0
- St. Louis (31)			50.0		80.0
Average		19.0	39.6	17.0	63.9
Standard Deviation		0.8	5.4	1.6	11.9
R-B - St. Louis (9)		16.0	31.0	15.0	54.0
- St. Louis (9)		17.0	33.0	17.0	55.0
- St. Louis (9)		16.0	29.0	13.0	53.0
- St. Louis (31)			40.0		60.0
- St. Louis (31)			35.0		68.0
- St. Louis (31)			34.0		60.0
- St. Louis (31)			28.0		55.0
Average		16.3	32.9	15.0	57.9
Standard Deviation		0.6	4.1	2.0	5.3
Midwest					
U-C - Charleston (21)[a]		55.0			104.0
- Charleston (26)[a]		33.4		27.1	97.0
- Chicago (28)[a]					86.5
- Cincinnati (28)[a]					74.3
- Charleston (43)[a]		33.1			
Average		40.5		27.1	90.5
Standard Deviation		12.6		-	13.0

(continued)

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TABLE 5 (continued)

	$D_{50} \leq 1\ \mu m$ Conc, $\mu g/m^3$	$D_{50} \leq 2.5\ \mu m$ Conc, $\mu g/m^3$	$D_{50} \leq 15\ \mu m$ Conc, $\mu g/m^3$	$D_{50} = 2.5 - 15\ \mu m$ Conc, $\mu g/m^3$	$D_{50} \leq 30\ \mu m$ Conc, $\mu g/m^3$
Southeast					
R-B - Elkmont (3)	24.0	56.0			
Average	24.0	56.0			
Standard Deviation	-	-			
Northeast					
U-C - NYC (12)			31.7		59.8
- NYC (12)					69.6
- NYC (14)	101.6[b]	103.1			105.8
- Philadelphia (28)[a]					58.5
- Washington, D.C. (28)[a]					56.3
- Boston (31)[a]			64.6		104.7
- NYC (43)[a]		64.5		42.6	
- Philadelphia (43)[a]		31.4		17.5	
Average	101.6	66.3	48.2	30.1	75.8
Standard Deviation	-	35.9	23.3	17.8	23.3
U-I - Buffalo (10)			61.0		76.62
- Buffalo (10)			64.0		76.21
- Lackawana (10)			74.0		100.54
- Buffalo (31)			92.0		115.50
Average			72.8		92.22
Standard Deviation			14.0		19.24
U-C - Buffalo (10)			53.0		68.93
- Lackawana (10)			70.0		-
Average			61.5		68.93
Standard Deviation			12.0		-

(continued)

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TABLE 5 (continued)

	$D_{50} \leq 1$ μm Conc, μg/m^3	$D_{50} \leq 2.5$ μm Conc, μg/m^3	$D_{50} \leq 15$ μm Conc, μg/m^3	$D_{50} = 2.5 - 15$ μm Conc, μg/m^3	$D_{50} \leq 30$ μm Conc, μg/m^3
R-B - Angola (10)			33.0		45.92
- Sterling Forest (12)			15.9		22.50
Average			24.5		25.7
Standard Deviation			10.1		14.4

a. Site classification not given in study. Classification assumed based on general knowledge of the area and relative concentration.

b. $D_{50} \leq 1.5$ μm.

NOTE: U = urban
            C = commercial
            I = industrial
        Res = residential
          S = suburban
          R = rural
          B = background

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(UCS) and manually constructing the branches of the decision tree using statistical information from INFORM.

The decision-tree analysis was used to explain the variation in the dependent variable (e.g., concentration for a given particle size) by sequentially splitting the data according to the independent variables (e.g., geographic area and site classification). An example of a decision tree is shown in Figure 6. The net result of the analysis is a decision tree that accounts for the variance in the dependent variable according to the groups defined by the independent variables.

Starting with the total number of sites which have data for a particular particle size and for the geographic or the site classifications, the data set was sequentially split into two subgroups of the independent variables. Each split was performed on the subgroup with the greatest variance. The split was selected to maximize the variance explained by that independent variable.

The results of the decision-tree analysis are in Table 6. For particles $\leq$ 2.5 μm, the urban-commercial site classification is the most important factor in explaining the variance (35.9%) in concentration followed by the NE geographic area classification (29.2%). The major reasons for this relationship is that particles $\leq$ 2.5 μm which make up a major portion of the transported aerosols are usually the products of fuel combustion or chemical conversion of gases or vapors and the major fuel combustion activities (including internal combustion engines) occur in highly populated areas in the NE which are also affected by transported aerosols.

For particles $\leq$ 15 μm, none of the independent variables seem to be significant in terms of explaining the variance. The highest percentage is for the NE and the rural-background site classification. However, in both of these cases the percentage of the variance explained was less than 20%. Also, the urban-industrial site classification and the NW geographic area classification were within a few percentage points of the variance explained by the rural-background site classification. Therefore,

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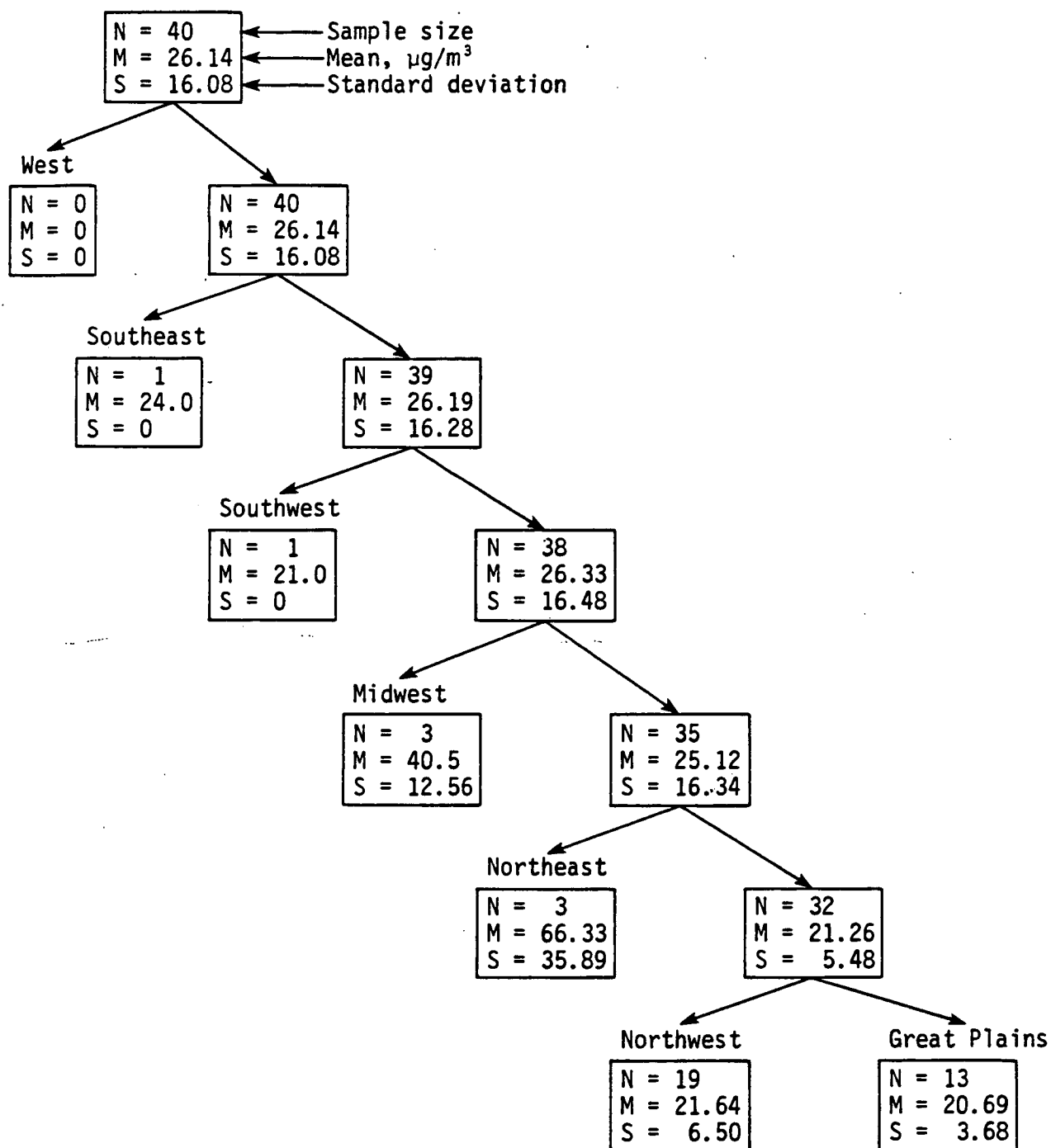
Figure 6. Example decision-tree, particles $\leq$2.5 µm versus geographic area.

TABLE 6. RESULTS OF DECISION TREE ANALYSIS

Percent Variance Explained[a]

Particle size (μm)	Geographic area							Site classification				
	NW	W	SW	GP	SE	MW	NE	U-C	U-I	S-C	S-Res	R-B
≤ 2.5	9.0	-	-	3.2	-	9.6	29.2	35.9	-	-	3.1	3.2
≤ 15	10.7	-	-	4.4	-	-	16.8	3.6	9.7	-	1.7	11.2
≤ 30	1.9	5.9	30.3	4.5	-	2.0	12.6	6.3	11.0	32.4	3.4	8.7

[a]Percent variance explained is the square of the correlation coefficient.

NOTE: U = urban
          C = commercial
          I = industrial
        Res = residential
          S = suburban
          R = rural
          B = background

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several variables seem to equally explain the variance in concentration for particles $\leq$ 15 μm. One explanation may be that particles $\leq$ 15 μm are products of mechanical processes which are not necessarily limited to certain areas of the country or to certain site types. It should be noted that both urban-industrial and rural-background sites are influenced by mechanical processes such as manufacturing operations in the case of industrial sites and the forces of the wind in the case of rural sites.

For particles $\leq$ 30 μm, the decision tree analysis indicates that 30.3% and 32.4% of the variance are explained by the SW and urban-commercial site classification, respectively, with the other variables individually explaining, in most cases, less than 10% of the variance. The results seem reasonable compared to other studies conducted over the past several years which have indicated that the concentrations in the SW are influenced by larger size particles and that most urban-commercial sites are influenced by streets and roadways near the monitoring site. In most cases the most significant PM emissions within a 1-mile radius of a urban-commercial monitoring site would be resuspension of PM from paved streets and the PM from unpaved streets, and parking lots. In general, the particle size associated with these PM sources would be 15 to 30 μm or larger.

In summary, the decision-tree analysis supports the observations made in Section 3.2 and 3.3. That is, the highest mean concentration for particles $\leq$ 2.5 μm is expected to occur at urban-commercial sites in the NE; the highest mean concentration for particles $\leq$ 15 μm is expected to occur at urban-industrial sites in the NE, although other sites in other areas of the country have similar values; and the highest mean concentration for particles $\leq$ 30 μm is expected to occur at urban-commercial in the W, GP and SW.

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SECTION 4.0

CHEMICAL CHARACTERIZATION

This section discusses the chemical composition data in the studies included in this analysis, the concentration of each major chemical component according to particle size ($\leq$ 2.5 μm, > 2.5 μm and $\leq$ 30 μm), and the variability of the chemical composition data due to seasonal factors and other influences.

4.1 ELEMENTS FOR WHICH DATA WERE AVAILABLE

Table 7 summarizes the chemical composition data contained in the studies included in this analysis. As can be seen from Table 7, a wide variety of chemical composition data were available from these studies. Not every study, however, reported data for every chemical element or component. In general most studies reported data on sulfate ($SO_4^=$), nitrates (NO_3^-), sodium (Na), magnesium (Mg), aluminum (Al), silicon (Si), sulfur (S), chlorine (Cl), potassium (K), calcium (Ca), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), bromine (Br), and lead (Pb). Additionally, some studies reported data on amonium (NH_4^+); elemental, organic, or total carbon (C); flourine (F), scandium (Sc), cobalt (Co), arsenic (As), selenium (Se), cadmium (Cd), antimony (Sb) and barium (Ba). Finally, a few studies reported data on hydrogen ion (H+), lithum (Li), rubidium (Rb), strontium (Sr), iodine (I), and cesium (Cs). None of the studies reported data on molybdenium (Mo) which is sometimes reported with the above elements. Because only one study included data on organic carbon and other organic compounds, a further review of the literature was conducted to obtain some additional data. Three additional studies were identified that provided organic data.

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TABLE 7. SUMMARY OF CHEMICAL DATA

Reference No.	H+	SO_4^-	NO_3^-	NH_4^+	Li	Carbon elemental	Carbon organic	Total carbon	F	Na	Mg	Al	Si	S	Cl	K	Ca	Sc	Ti	V	Cr	Mn	Fe
1		e	e	e						e	d	e	f		d	e	e		c			c	e
3											c		d	c	a	c	c		c	a			c
5																							
6										c			c	e			c						
7			a,b							c,d,e	b,c	c,d	e	d,e	b,c,d,e	c,e	c,d,e		b,c	a,b		b	c,d,e
8													c,d	c,d,e									
9													d,e	e	e		e		b,c,d	a			d,e
10	f	e	f			d			b,c	c,d		e	f	e,f	c,d	c,d,e	e			a,b	a	b,c	c,e
13		f		e						c	b	d	d	e		b	c		b	a		a	c
14																				c	b	b	e
16		e	e					b,c		d,e	c,d,e	e	f	e	e	c,d	d,e		c	a	b	b,c	d,e
17					f					d	c	e	f	d	c	d	d		c	b	b	b	e
19										d,e,f	c,d,e	e			c,d	c,d,e	d,e			a	a,b	b	e
20		e	e	e	a					e	e	f	f			e	f		c		a	b	e

(continued)

TABLE 7 (continued)

Reference No.	Co	Ni	Cu	Zn	As	Se	Br	Rb	Sr	Mo	Cd	Sn	Sb	I	Cs	Ba	Pb	AA	Flame photo.	XRF	PIXE	GC	Neutron activation	Ion exp XRF	Ion chromatography	Other
1		b	d				b										c									
3		a	a	a	a	a	a										c					X				
5																	c,e				X					
6																	e				X					
7			a,b	b,c			b,c										c,d, e							X		
8		b															b				X					
9																	c,d									
10		a,b		b,c			c,d, e										c,d			X					X	
13			b			a	b				a					a	b			X			X		X	
14		c	b	c							a						e			X						X
16		b	b	b,c	a	a	b,c				b					b	c,d, e			X			X		X	
17		a	c	b			b										c			X						
19		a,b	b,e	a,b			c,d e							a			e			X			X			X
20		a	c	c				b	b		a						d	X								

(continued)

TABLE 7 (continued)

Reference No.	H+	SO$_4^-$	NO$_3^-$	NH$_4^+$	Li	Carbon elemental	Carbon organic	Total carbon	F	Na	Mg	Al	Si	S	Cl	K	Ca	Sc	Ti	V	Cr	Mn	Fe
21		f	d,e										e,f	e,f			d,e		b,c				d,e
22		e,f	e																			b	c,e
26								f		c		e	e	e	c	c	e		b			b	d
27		f	e	d						c	c	e			c	d	d	a	c	b	b	b	e
32		e	e	e						e		e	e	e		e	d		c	b		a	e
35		e	e			e	f		c	e	d	e	f	e	e	d	e	a	c	b	b	c	e
36										e		d,e						a		d,e		b	d,e
37										e		d,e			e			a		b,d		b	d,e
40		f	e	e						c,d	c	c,d			c	c		a	b	a,b	a	c,d	
42										e		d,e f	e,f		e	d		a		a	a	b	e
43										d,e f		d,e f	e	e	c,d	c	d,e		b	b,c	b	b	d
44													f	f		e	f			e			e
46		f	d	e								d,e	e,f			d	d		c				d

(continued)

TABLE 7 (continued)

Reference No.	Co	Ni	Cu	Zn	As	Se	Br	Rb	Sr	Mo	Cd	Sn	Sb	I	Cs	Ba	Pb	AA	Flame photo.	XRF	PIXE	GC	Neutron activation	Ion exp XRF	Ion chroma- tography	Other
21			b	b,c		a,b	b,c										c,e	X		X	X				X	X
22				b,c	a,b						a,b						c			X					X	
26			b	b	c	a	c		a								d			X					X	
27	a	b	b	c	a	a	c				a		a	a		b	d,e	X					X			
32				c			d									b	e			X					X	X
35	a	b	b	c		a	c						b				d		X	X			X		X	
36	a			c		a	c						a,b										X			
37	a		b,c			a							a										X			
40	a		b	c	a	a	c				a		a,b	a,b	a	b	c,d	X				X	X			
42	a	a		c		a	c				a		a				d									
43			b	c			c		a								e			X					X	
44				c			c										e			X					X	
46			b				c										d			X					X	

Note: Concentration Ranges, µg/m³

$0.0 < a \leq 0.01$
$0.01 < b \leq 0.10$
$0.10 < c \leq 0.50$
$0.50 < d \leq 1.00$
$1.00 < e \leq 5.00$
$5.00 < f$

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Table 7, indicates the relative concentration ($\mu g/m^3$)
reported for each element or component for particles $\leq$ 30 μm by
using the following notation:

$$\mu g/m^3$$

$$0.0 \ \leq a \leq 0.01$$
$$0.01 \leq b \leq 0.10$$
$$0.10 < c \leq 0.50$$
$$0.50 < d \leq 1.00$$
$$1.00 < e \leq 5.00$$
$$5.00 < f$$

With the exception of $SO_4^=$, NO_3^-, NH_4^+, Al, Si, Fe, and Pb, the
reported concentrations were < 1.0 $\mu g/m^3$. Many concentrations
were < 0.1 $\mu g/m^3$. Concentrations for components such as V, Sc,
CO, Se, Sr, Cd, Sb, and I were $\leq$ 0.01 $\mu g/m^3$, with many concen-
trations $\leq$ 0.005 $\mu g/m^3$ and some < 0.001 $\mu g/m^3$. In most cases,
the major chemical components (in terms of total concentration)
were $SO_4^=$, NO_3^-, and Si, followed by Al, Fe, and Pb.

4.2 ANALYTICAL TECHNIQUES USED IN THE STUDIES

Table 7 lists the analytical techniques used to determine
the chemical composition of the PM in each study. In many cases,
more than one technique was used in each study. The most commonly
used techniques were X-ray fluorescence (XRF), ion chromotography,
and neutron activation. A few studies also used atomic absorption
and particle-induced X-ray emission (PIXE).

X-ray fluorescence[25,26] has been used in a number of studies
over the last 7 to 10 years. Its low detection limit for elements
with atomic numbers of 13 and greater and its simultaneous multi-
element capability make it a valuable tool in analyzing the
chemical composition of PM.

In the XRF technique, atoms are excited from ground state to
higher energy levels by X-radiation from an X-ray tube. These
excited atoms emit discrete energy X-rays as they return to their
normal ground state energy levels. Each element has a character-
istic X-ray pattern that is used to identify the element. The

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number of the X-rays observed, which is proportional to the number of atoms, is used to determine the concentration of the element through a direct comparison with a standard reference.[27]

The XRF analysis technique has demonstrated a capability for quantitative analysis of up to 18 elements commonly found in urban PM; the 18 are Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Sr, Zr, Mo, Cd, Sn, Ba, and Pb. The XRF can also provide semi-quantitative analysis of up to nine low atomic-number elements; Na, Mg, Al, Si, P, S, Cl, K, and Ca. Of the 18 elements listed as being quantitatively measured in an urban area, three are mea-sured occasionally (Ni, Mo, Sn), two are questionable in terms of absolute atmospheric detection (Se, Cd) and two are often affected by interferences from other elements--that is, Ba and Ti interfere with the ability to quantify V and Pb interferes with As. The Pb also interferes with the ability to quantify S (40 ng/m^3 detection limit) even though S is one of the elements that can be detected but not quantitatively measured by XRF.[28]

For XRF, the lower limits of detection and the capability for a quantitative analysis of element concentration are dependent on the sampling procedure. The lower limits depend primarily on the volume of air sample per square centimeter of collection sub-strate and substrate mass per square centimeter. The capability to quantify an element is related to the depth of deposition within the sampling media and to the total loading per square centimeter.[28]

Instrumental neutron activation is a nondestructive multi-element technique that has been used in a number of PM studies over the past several years. When a sample is placed in a neutron flux from a nuclear reactor, the elements in the sample absorb neutrons and form radioactive elements. The number of radionuclide atoms created for each species is proportional to the number of atoms originally present. The intensity of gamma radiation emitted by these atoms is not only proportional to the number of radionuclide atoms present but also occurs at an energy level unique to that radionuclide. The specific radioactivity produced

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from the sample is compared with that from a standard to quantitatively determine the concentration of the element in the sample.[27] A PM sample contains many elements and occasionally several isotopes of the same element, therefore, the activation or counting technique must be chosen to optimize the activity of as many elements as possible. In many studies, this involved two or more irradiations for each sample and applying various counting schedules. Table 8 presents an irradiation and counting strategy designed to give the maximum sensitivity for a wide range of elements. The elements detected for each strategy are also presented.[29]

Instrumental neutron activation is often used to supplement the results of XRF because several elements (e.g., Na and Mg) cannot be detected by XRF at their normal concentration levels. Instrumental neutron activation is also a useful tool in validating results from using other analytical techniques.

Ion chromatography developed by Small[30] was used in several PM analyses; however, it is still a relatively new technique in comparison to XRF or instrumental neutron activation. The basic principle is similar to that used in all chromatographic techniques. A sample is extracted in a known amount of solvent to which all soluble elements or species are transformed. The sample is injected into the chromatograph and passes through a separator column containing a strong base anion exchange resin. This resin has the ability to separate the anions by differences in their bonding strengths. The resin performs the separating function for anions only in the presence of cations. In ion chromatography, the ions are removed and converted to their acid forms by passing through the ion exchange resin. The conductivity cell in the chromatograph detects only the current passed by the ions of each acid as they are separated over time. The currents measured are proportional to the number of ions present. The current generated by the sample is compared to the current generated by a prepared standard to quantify each element. Five ions (F^-, Cl^-, Br^-, NO_3^-,

TABLE 8. NEUTRON IRRADIATION AND SAMPLE COUNTING SCHEDULE[29]

Irradiation time, flux	Cooling time	Counting time	Elements detected
2 min, 2×10^{13} n/cm² sec	4 min	500 sec (Q1)[a]	Al, V, Cu, Ti, Ca
	20 min	1000 sec (Q2)[b]	Na, Mg, Cl, Mn, Br, I, Ba, In
12 hr, 5.1×10^{12} n/cm² sec	20-30 hr	40 min (LI)[c]	Eu, Br, As, W, Ga, Zn, K, Cu, Na, Cd
	6-10 days	80 min (L2)[d]	Sm, Au, Hg, La, Sb
	20-30 days	600-800 min (L3)[e]	Fe, Cr, Co, Zn, Hg, Se, Ag, Sb, Ce, Eu, Sc, Th, Ni, Ta, Hf, Ba, Rb, Zr, Cs, Yb, Tb, Lu

[a]First count after short irradiation.
[b]Second count after short irradiation.
[c]First count after long irradiation.
[d]Second count after long irradiation.
[e]Third count after long irradiation.

and $SO_4^=$) are generally considered to be quantifiable with ion chromatography.

Atomic absorption spectroscopy is a powerful tool for the determination of most metals in the atmosphere. In 1955 Walsh[31] first recognized the potential advantages of atomic absorption over other methods, and devised a simple instrument for analyzing a wide variety of elements. Since then considerable work has been done to further develop the technique and to apply it to a number of situations. In most cases, ground state atoms make up the bulk of the atomic population. These atoms absorb radiation at discrete wavelengths characteristic of each element. If these atoms are excited, they emit radiation as they return to the ground state. The amount of energy absorbed and emitted is a function of the number of atoms in the sample. These data can be used to identify and measure the concentration of the elements in the sample.

An atomic absorption spectrometer has a radiation source, usually a hollow cathode lamp, that has an emitter cathode made of the element to be determined. Vapor discharge lamps can be used in place of the hollow cathode sources for certain elements. The sample to be measured is atomized in a flame by conventional atomizers and a burner. The radiation from the source traverses the flame and is directed into the split of a monochromator that separates the desired resonance lines from other lines in the sample. The intensity is measured by a photomultiplier tube and amplifier. The flame, however, also emits radiation at the same wavelength as the sample. This background radiation is considered by modulating the radiation from the source and sending the signal from the detector to a tuned ac amplifier that rejects dc signals emitted from the flame. The modulation is accomplished by chopping the light beam.

Atomic absorption spectroscopy is relatively free from physical and chemical interferences. The main disadvantage is that it cannot be applied to nonmetals because their resonance lines are below the vacuum ultraviolet region.[32]

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In flame atomic absorption, the elements pass rapidly into the flame thereby limiting the lifetime to a few thousands of a second. These atoms recombine in the cold zones and can produce simple and double oxides and hydroxides as well as stable compounds. Therefore, the atomization yield in flames is always low. Other methods have been investigated for decomposing the sample. These methods are the same as flame atomic absorption except that a nonflame atomization source replaces the atomizer-burner. Using a nonflame source, the technique can determine element concentrations much lower than those determined by classical atomic absorption. A nonflame analysis is recommended for Cu, Ni, Pb, Cd, Be, and As. The flame analysis is used for Al, Mn, Fe, V, Mg, Zn, and Ca.[33]

4.3 TYPICAL CONCENTRATION RANGES

Concentrations of the major PM elements varied from study to study (Table 7). As expected, the concentrations also varied from site to site within a particular study. In those cases where a study contained data for more than one site and the concentration varied significantly from site to site, one or more concentration ranges (footnotes a-f), were shown in Table 7 to reflect the variation in the concentration. Although there is considerable variation in the concentration data for some elements, other elements, for the most part, fall within a given concentration range.

Figure 7 summarizes the concentration ranges and the typical or mean concentration for each of the major elements or chemical components in the studies included in this analysis. With exceptions (NO_3^-, $SO_4^=$, NH_4^+, Al, Si, S, Cu, and Fe), most elements or chemical components have a typical or mean concentration of < 1.0 $\mu g/m^3$. Of those chemical components with mean concentrations > 1.0 $\mu g/m^3$ (NO_3^-, $SO_4^=$, NH_4^+, Al, Si, S, Cu, and Fe), only $SO_4^=$ has a mean concentration > 6.0 $\mu g/m^3$. Only three components ($SO_4^=$, Si, and S) had maximum concentrations > 10.0 $\mu g/m^3$; most
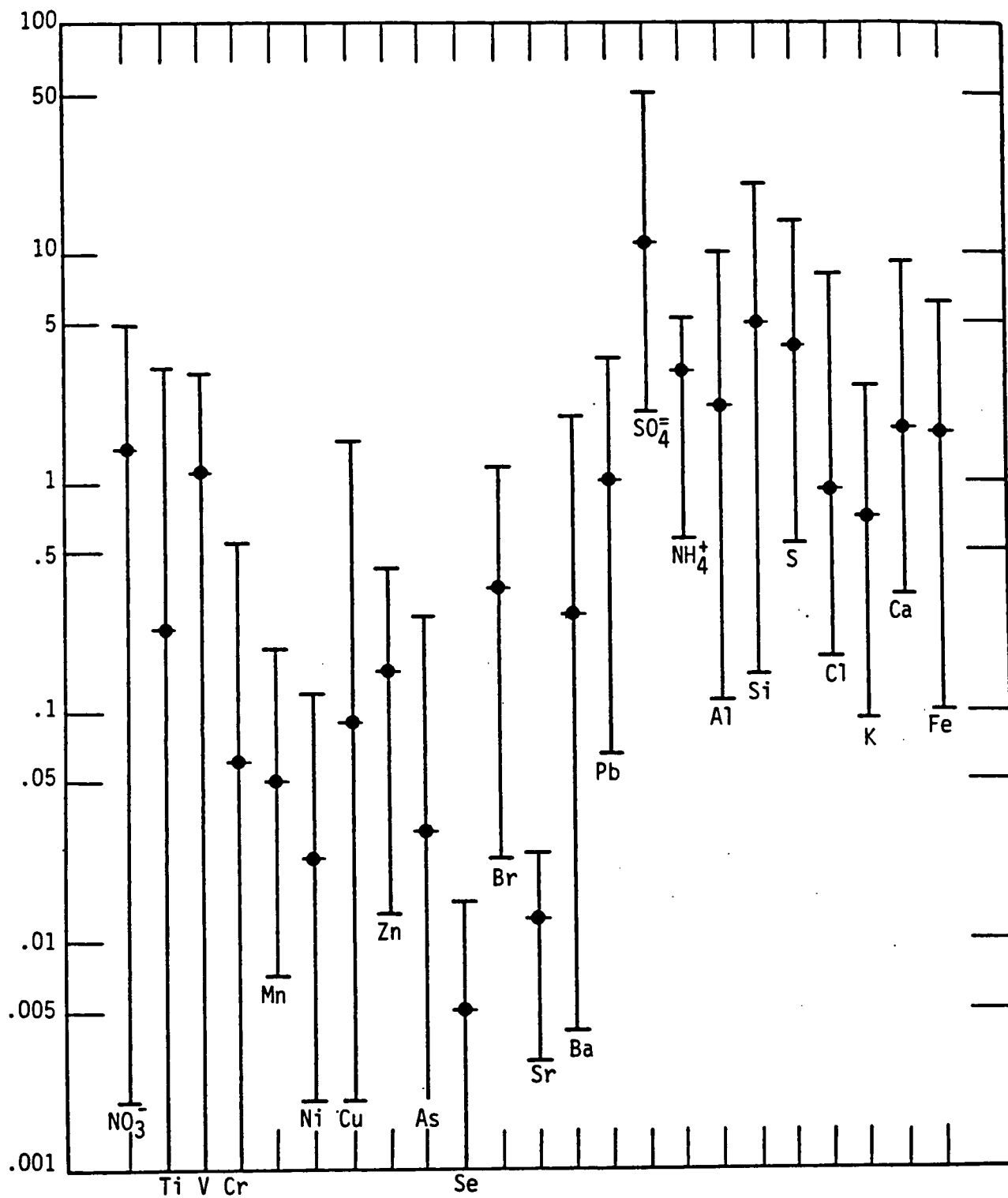
Figure 7. Typical concentration ranges.

maximums were < 1.0 µg/m^3. In reality only two chemical components have maximum concentrations > 10 µg/m^3--SO$_4^=$ and Si. Since there is very little SO$_3^-$ and elemental S in the atmosphere, the S identified in most studies would be SO$_4^=$. Therefore, if the S concentration is multiplied by 3 it would be a reasonable approximation of the SO$_4^=$ concentration that would have been measured for that particular study.

To determine whether the concentration ranges (Figure 7) were representative, the ranges were compared to data from previous studies or to compilations on typical concentration ranges for elements in urban aerosols. Figure 8 summarizes the data from a compilation[27] for the same elements or chemical components included in this analysis.

Figures 7 and 8 indicate that, in general, the mean or typical concentrations in the studies in this analysis were consistent with typical concentrations in a previous compilation. In all cases, the typical concentrations were in the same order of magnitude. Generally, the typical concentrations and the maximums and minimums in Figure 8 are slightly higher than those in Figure 7. The tendency for the higher concentrations in Figure 8 may be explained by the fact that Figure 7 is a compilation of aerosol data for all site classifications (urban, suburban, and rural) whereas Figure 8 includes only urban aerosol data. For most chemical components, the concentrations observed at urban sites tend to be somewhat higher than for other site classifications. However, the data for many of the major chemical components are quite consistent for the variety of sites and geographic locations.

Ambient PM concentrations usually have two major categories or physical components. The first category is commonly called the background. Background concentration has many components including windblown dust from natural surfaces, biological debris, and long-range transport of both primary and secondary aerosols. Background is usually measured at a nonurban site that is unaffected by nearby emission sources. Background concentrations
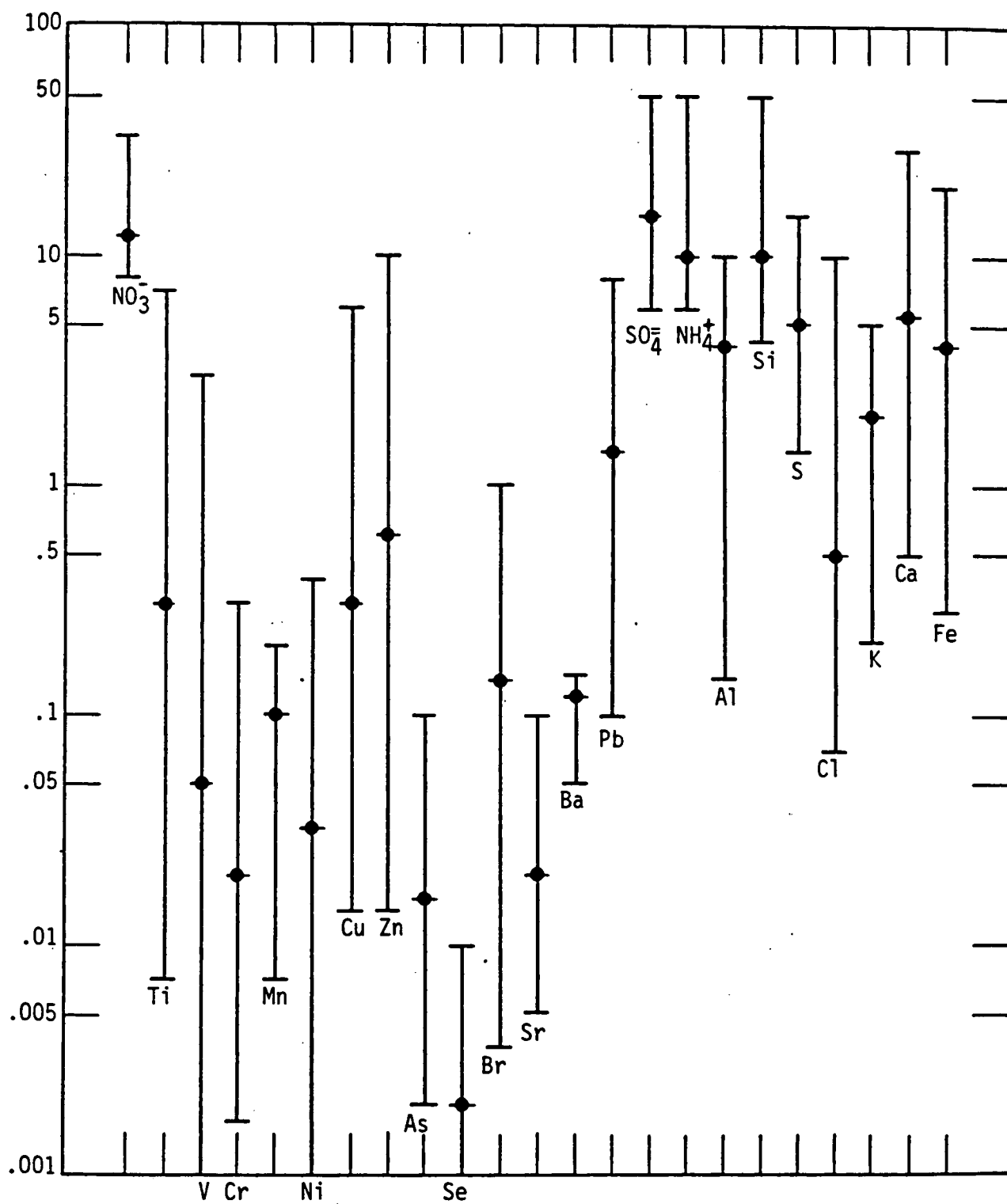
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Figure 8. Typical concentrations for urban aerosols.

are defined in 40 CFR 51.13 as "that portion of the measured ambient levels of particulate matter that cannot be reduced by controlling emissions from manmade sources; background concentration shall be determined by reference to measured ambient levels of particulate matter in nonurban areas." Nonurban background levels include natural particulate (particulate from natural processes and thus uncontrollable); transported particulate (particulate levels due to emissions from man's activities in "upwind" urban area); and local particulate.

The second category is commonly referred to as "urban." This includes two subparts: first, locally emitted $SO_4^=$, NO_3^-, and various organics that form secondary aerosols, and second, the areawide emissions from fugitive dust and industrial sources. The fugitive dust, or soil related sources can account for well over half of the ambient aerosol at a site. Table 9 lists the typical concentrations of trace elements from rocks and soils.[34]

Although the earth's crust is the direct source of many of the trace elements in the atmosphere, industrial and agricultural activities sometimes make direct use of large quantities of trace elements or these elements are a major component of the raw material being processed. Table 10 lists the annual emission estimate of trace elements in the atmosphere.[34,36] Although the values in Table 10 are only rough estimates, they do indicate that various elements can have a significant impact in terms of their overall emissions as a percentage of the total trace element emissions.[34]

One possible stationary source of trace elements is the combustion of coal at utility and industrial boilers. Coal can contain a variety of elements. The concentrations of the elements depend on the location of the coal seam and on the method of cleaning the coal prior to use. Table 11 compares the initial trace element concentrations in coals by geographic region.[37]

Certain elements have been used as tracers to determine the potential sources of PM. Table 12 lists the source categories

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TABLE 9. TRACE ELEMENT CONCENTRATIONS (ppm) IN ROCKS AND SOILS[34]

Elements	Rocks-granite	Sedimentary rocks	Earth soils
Ag	0.040	0.900	0.100
As	1.500	6.000	5.000
Au	0.004	0.001	0.001
B	10.000	12.000	10.000
Ba	600.000	80.000	500.000
Be	2.000	3.000	6.000
Bi	0.001	1.000	1.000
Cd	0.100	0.300	0.600
Ce	60.000	50.000	50.000
Co	2.000	20.000	8.000
Cr	8.000	150.000	200.000
Cs	2.000	12.000	5.000
Cu	10.000	60.000	20.000
Ga	15.000	30.000	30.000
Hg	0.050	0.400	0.010
La	50.000	40.000	40.000
Li	30.000	60.000	30.000
Mn	400.000	700.000	800.000
Mo	1.200	1.000	2.000
Ni	5.000	100.000	40.000
Pb	20.000	20.000	10.000
Rb	170.000	200.000	100.000
Se	0.050	0.600	0.010
Sn	3.000	30.000	10.000
Sr	200.000	400.000	300.000
Ti	4000.000	4000.000	5000.000
Tl	2.000	1.000	
U	3.000	3.000	1.000
V	40.000	130.000	100.000
W	2.000	1.000	
Y	30.000	30.000	50.000
Zn	40.000	80.000	50.000
Zr	170.000	200.000	300.000

TABLE 10. ANNUAL EMISSIONS OF TRACE ELEMENTS IN THE ATMOSPHERE[34,36]

Elements	Emission, tons/yr	Emission, %
Arsenic	10,600	1.60
Barium	15,420	2.33
Beryllium	172	0.03
Cadmium	2,160	0.33
Chromium	18,136	2.73
Copper	13,680	2.07
Lead	230,000	34.72
Manganese	17,900	2.70
Magnesium	75,293	11.38
Mercury	857	0.13
Molybdenum	990	0.14
Nickel	7,310	1.10
Selenium	986	0.14
Silver	417	0.06
Titanium	88,351	13.33
Vanadium	20,300	3.07
Zinc	159,922	24.14

TABLE 11. COMPARISON OF INITIAL CONCENTRATIONS OF TRACE ELEMENTS IN COALS BY GEOGRAPHICAL REGION[37]

	Concentration, ppm			
	Average, 20 coals	East	Midwest	West
Sb	1.01	0.91	1.73	0.83
As	12.10	15.70	9.95	4.70
Be	1.90	2.49	1.75	0.54
Cd	0.57	0.10	3.31	0.06
Cr	29.60	39.80	25.40	7.61
Co	6.27	8.59	5.12	1.40
Cu	18.10	24.10	11.20	7.75
F	146.00	186.00	132.00	58.30
Pb	13.70	14.30	27.30	4.03
Mn	67.30	62.80	137.00	36.50
Ni	18.40	23.90	18.70	4.84
Se	2.82	3.67	2.45	1.02
V	44.40	57.80	48.30	10.00
Zn	57.80	33.20	238.00	9.20
Si	61,300.00	80,200.00	51,000.00	22,200.00
Al	29,300.00	40,400.00	19,100.00	8,680.00
Fe	14,400.00	15,800.00	24,600.00	4,930.00
Ca	5,750.00	2,690.00	8,240.00	11,600.00
Mg	2,300.00	2,330.00	1,640.00	2,610.00
Ti	1,520.00	2,050.00	1,070.00	532.00
Na	976.00	741.00	990.00	1,530.00
K	5,340.00	7,640.00	4,000.00	641.00

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TABLE 12. TRACERS USED IN POTENTIAL SOURCE IDENTIFICATION[38]

Source type	Dominant particle size	Major chemical species[a]
Geological		
Rock crusher, grinding	coarse	Al,Si,Fe,Ti
Asphalt roofing material	coarse	Al,Si,Fe,Ti
Street dust	coarse	Al,Si,Fe,EC,OC,Ti
Concrete batching	coarse	EC,OC,Ca,$SO_4^=$,Na, Cl
Abrasives	coarse	EC,OC,CA
Transportation		
Auto leaded gas	fine	Pb,Br,Cl,EC,OC
Auto unleaded gas	fine	EC,OC
Diesel truck	fine	EC,OC
Diesel train	fine	EC,OC
Fossil Fuel		
Residential oil combustion	fine	EC,OC,V,Ni,$SO_4^=$
Distillate oil combustion	fine	EC,OC,$SO_4^=$
Anthracite coal combustion	fine	Al,Si,Fe,Na,OC, EC,As
Natural gas combustion	fine	EC,OC
Bituminous coal combustion	fine	EC,OC
Fuel oil combustion	fine	EC,OC
Refinery gas combustion	fine	EC,OC
Forest Products Industry		
Wood products	coarse	EC,OC
Paperboard container manuf.	coarse	EC,OC
Bark boiler	fine	EC,OC
Bark dryer	fine	EC,OC
Vegetation		
Feed & grain handling	coarse	EC,OC,SI
Heavy Industry		
Refinery oil heater	fine	EO,OC,V
Coke oven	fine	EO,OC
Mineral handling	coarse	EO,OC,Mn,Al,Si,Fe
Copper smelting	fine	Cu,Al,S,Pb,Zn
Lead smelting & production	fine	Pb,S,Na,Cl,Fe

(continued)

TABLE 12 (continued)

Source type	Dominant particle size	Major chemical species[a]
Aluminum smelting	fine	Al,F
Zinc galvanizing	fine	Zn
Iron & steel foundries	fine	Fe,Zn,Cu,Cr,Mn
Aluminum melting furnace	fine	S,Al,K,Na,Cl,Fe
Blast furnace	fine	Fe,Mn,Zn
Carbon black furnace		EO,OC
Miscellaneous		
Incinerator	fine	OC,EC,Zn,Pb,Al, Cl,Cd,Cu

[a]EC = elemental carbon
 OC = organic carbon

and the tracers that have been used to determine the potential sources of PM.[38]

Only one study listed in Table 7 included data on organic carbon and other organic compounds. A further review of the literature associated with some of these studies provided some limited data on organic compounds from the New York City Summer Aerosol study;[39] sampling conducted by the New York University Medical Center in 1968-1969 and 1977;[40] and the Aerosol Characterization Experiment conducted in California.[41]

Particulate organic matter (POM) is a complex mixture of many different individual compounds. These compounds can include alkanes, alkenes, polycyclic aromatic hydrocarbons, phenols, esters, nitrocompounds, and sulfur heterocyclic compounds. In some cases POM can constitute a significant fraction of PM in the urban aerosol.

The ultimate source of most POM in the urban aerosol appears to be fuel combustion. However, the ability to identify the contributions of various sources to the total amount of POM in the urban aerosol is very limited. As with inorganic compounds, the estimates of source contributions have been based mainly on emission inventories. Studies of long-term trends in ambient POM concentration can provide some indication of the sources and their relative significance. For example, the TSP in New York City has declined about 40% between 1968 and 1978, however the decline in POM has only been about 16%. The decline in TSP is due principally to the burning of cleaner, low-ash, low sulfur oil. As illustrated in Table 13, the use of low-sulfur fuels has not led to a proportional reduction in POM. In contrast to the data from New York, the decline in the POM concentrations in Los Angeles have corresponded to the decline in the TSP concentrations due to the fact that over the past ten years the regulations in Los Angeles have been directed toward the control of hydrocarbon emissions from automobiles.[40]

One of the primary objectives of the summar aerosol study was to investigate the nature of the organic fraction of the New

TABLE 13. ANNUAL AVERAGES OF ORGANIC FRACTIONS IN TOTAL SUSPENDED PARTICULATE MATTER, NEW YORK CITY,[a] DISPERSION-NORMALIZED[40]

Year	TSP ($\mu g/m^3$)	Organic fraction[b] ($\mu g/m^3$)	Percent organics in TSP
1968	95.7	10.2	10.6
1969	128	10.8	8.4
1977-1978	59.8	8.8[c]	14.7

[a]NYU Medical Center Station

[b]Total of nonpolar (benzene-soluble) and polar (acetone-soluble) organics.

[c]Respirable ($\leq 3.5\ \mu$) organics only.

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York City aerosol. Figure 9 summarizes the aerosol concentrations of TSP and organic solvent extracts of TSP observed during the summer aerosol study. Nonextractable carbon was determined for three of the samples that had been sequentially extracted. Table 14 summarizes the results of carbon analysis. Although the values in Table 13 are somewhat less than the values found for extractable organic compounds, they are of the same order of magnitude.[39]

Data available on the chemical analysis of aerosols in several California cities[29] indicate that the total benzene soluble organic concentrations ranged from 2.0 to 15.2 $\mu g/m^3$ which represented 10% to 16% of the total PM.

4.4 PARTICLE SIZE RANGES FOR EACH MAJOR CHEMICAL COMPONENT

Several studies included in this analysis presented data on PM size and chemical composition. Three particle sizes were used in presenting the chemical composition data--$\leq$ 2.5 μm, > 2.5 μm, and $\leq$ 30 μm. Table 15 summarizes the chemical composition data by particle size. The mean, SD, and minimum and maximum values for each major component for each of the above specified particle sizes are presented. Although considerable data were available for particle sizes $\leq$ 30 μm, less data were available for the other two sizes. Table 15 indicates a considerable range of the element concentrations for all three particle sizes reported. It should, however, be pointed out that all site classifications and geographic areas are combined in Table 15--that is, rural data were combined with urban data, and NW data combined with NE data. Therefore, there was a rather wide difference between the minimums and maximums.

The data for particle diameters $\leq$ 2.5 μm indicate that this size range is dominated by $SO_4^=$ (34.34 $\mu g/m^3$), followed by S, NO_3^-, and NH_4^+, and Pb. The other components have similar concentrations with almost all the values < 0.5 $\mu g/m^3$; several components have concentrations $\leq$ 0.1 $\mu g/m^3$.
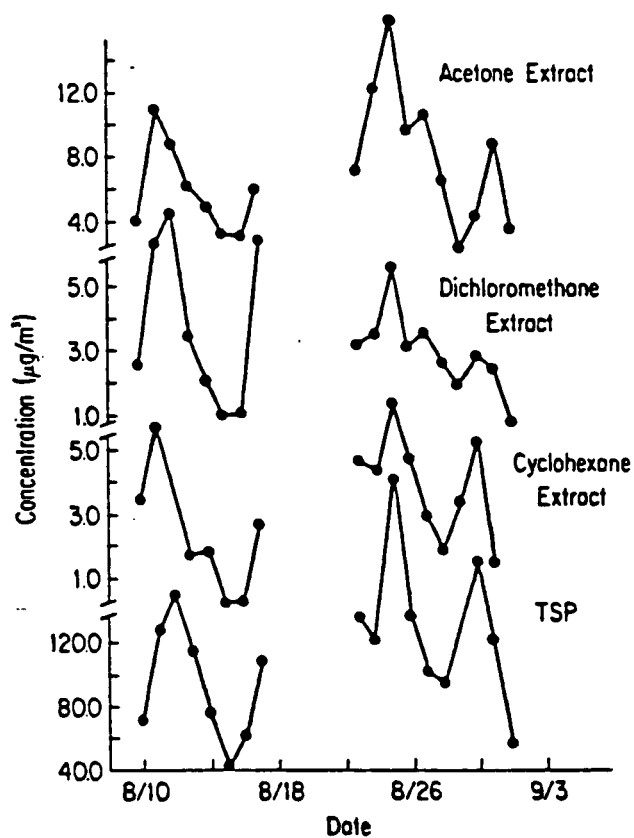
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Figure 9. Aerosol concentrations of TSP and organic solvent
extracts of TSP observed in New York City
during NYSAS-1976.[39]

TABLE 14.   CARBON-CONTAINING FRACTIONS OF THE
AMBIENT AEROSOL, NYSAS-1976[39]

Date	Extractable Organics[a]		Nonextractable Organics[b]	
	$\mu g/m^3$	%TSP	$\mu g/m^3$	%TSP
8/30-8/31/76	12.1	7.2	4.6	2.7
8/31-9/10/76	12.5	10.0	6.5	5.0
9/01-9/02/76	4.4	8.0	3.1	5.6

[a]Sum of material extracted with cyclohexane, dichloro-
methane, and acetone.

[b]Measured as elemental carbon.

TABLE 15. CHEMICAL CONCENTRATION BY PARTICLE SIZE

Component	$D_{50} < 2.5\mu m$ Mean, μg/m³ (SD)[a]	Minimum, μg/m³	Maximum, μg/m³	$D_{50} > 2.5\mu m$ Mean, μg/m³ (SD)[a]	Minimum, μg/m³	Maximum, μg/m³	$D_{50} < 30\mu m$ Mean, μg/m³ (SD)[a]	Minimum, μg/m³	Maximum, μg/m³
$SO_4^=$	34.34 (27.15)	3.00	50.83	1.96 (1.63)	0.69	3.80	11.00 (13.76)	2.04	50.58
NO_3^-	2.66 (1.25)	1.90	4.1	1.69 (1.77)	0.34	4.20	1.49 (1.53)	b	5.00
NH_4^+	2.13 (0.40)	1.71	2.5				3.11 (1.33)	0.56	5.32
AL	0.37 (0.60)	0.02	1.98	1.88 (2.57)	0.33	8.68	2.04 (1.78)	0.12	10.66
Si	0.41 (0.28)	0.04	1.00	3.82 (3.03)	0.58	10.13	5.71 (4.47)	0.14	20.00
S	4.92 (4.19)	1.40	12.60	0.65 (0.48)	0.35	1.50	3.44 (2.84)	0.53	13.90
CL	0.17 (0.15)	0.01	0.48	0.50 (0.42)	0.01	0.72	0.94 (1.29)	0.02	7.90
K	0.25 (0.26)	0.04	1.00	0.62 (0.53)	0.11	1.50	0.68 (0.52)	0.09	2.60
Ca	0.20 (0.21)	0.02	0.36	1.79 (2.27)	0.32	8.20	1.77 (1.47)	0.33	8.90
Ti	0.11 (0.31)	0.01	1.10	0.26 (0.55)	0.02	2.00	0.23 (0.45)	c	3.10
V	0.05 (0.07)	0.01	0.21	0.02 (0.03)	b	0.08	0.09 (0.23)	c	1.03
Cr	0.01 (0.01)	d	0.03	0.01 (0.01)	b	0.02	0.06 (0.15)	c	0.64
Mn	0.02 (0.02)	0.01	0.05	0.02 (0.02)	0.01	0.04	0.05 (0.04)	0.01	0.20
Fe	0.29 (0.37)	0.03	0.38	1.14 (1.22)	0.12	1.44	0.17 (1.16)	0.10	6.20
Ni	c			c			0.02 (0.02)	b	0.12
Cu	0.04 (0.03)	e	0.07	0.02 (0.01)	0.01	0.04	0.09 (0.24)	b	1.50

(continued)

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TABLE 15 (continued)

Component	D$_{50}$ <2.5µm Mean, µg/m³ (SD)[a]	Minimum, µg/m³	Maximum, µg/m³	D$_{50}$ >2.5µm Mean, µg/m³ (SD)[a]	Minimum, µg/m³	Maximum, µg/m³	D$_{50}$ <30µm Mean, µg/m³ (SD)[a]	Minimum, µg/m³	Maximum, µg/m³
Zn	0.12 (0.12)	0.05	0.37	0.06 (0.06)	d	0.20	0.15 (0.14)	0.01	0.46
As	b			b			0.03 (0.07)	b	0.26
Se	c			c			0.01 (d)	c	0.02
Br	0.28 (0.21)	0.02	0.72	0.07 (0.06)	0.01	0.19	0.35 (0.29)	0.02	1.19
Sr	e (d)	c	0.01	0.01 (d)	b	0.01	0.01 (0.01)	e	0.02
Ba	0.07						0.26 (0.54)	d	1.48
Pb	1.08 (0.64)	0.10	2.04	0.27 (0.21)	0.01	0.50	0.99 (0.71)	0.06	3.34

[a]Standard deviation.

[b]0.002.

[c]0.001.

[d]0.004.

[e]0.003.

NOTE: Concentrations are not additive either horizontally or vertically.

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The data for particle diameters > 2.5 μm indicate a slightly more uniform concentration distribution. Crustal elements like Si, Al, and Ca have concentrations equal to those of $SO_4^=$ and NO_3^-. No one component dominates this size range as $SO_4^=$ did for particle diameters ≤ 2.5 μm. A review of these data indicates that both primary and secondary particles have significant impacts and many types of sources may contribute to the particles > 2.5 μm.

The data for particle diameters ≤ 30 μm indicate that crustal elements Si, Al, Fe, and Ca dominate this size range. Although the combined concentrations of the four components is significant, the highest mean and maximum concentrations for all components were for $SO_4^=$ (11 μg/m³ and 50 μg/m³). The second highest mean and maximum concentrations were for Si (5.7 μg/m³ and 20 μg/m³). Again, both primary and secondary particulates influence particles ≤ 30 μm, and a variety of sources impact the overall PM concentration.

4.5 VARIABILITY OF CONCENTRATION BASED ON SEASONAL FACTORS OR OTHER INFLUENCES

The four major factors that affect the variability of the PM chemical composition are geographic area, monitoring site location, seasonal influences, and diurnal variability. The first two factors, geographic area and monitoring site location, are discussed in Section 3.0.

4.5.1 Diurnal Variability

Four of the studies included in this analysis had data on the diurnal variability as it relates to the PM chemical composition and particle size.[29,41,42,43] Three other studies were identified that also addressed the diurnal variation of aerosol trace element concentration.[40,44,45]

The first study[29] which examined the aerosol in California indicated that there was an afternoon peak for particles between .1 to 1.0 μm corresponding to a photochemically generated aerosol resulting from local emissions. The study also indicated that

there were significant diurnal changes in sulfur- and nitrogen-bearing compounds.

A second study[41] which was conducted in New York City showed that the diurnal pattern for particles < .1 μm closely followed the diurnal traffic pattern and to a lesser extent the summer diurnal power demand pattern. The diurnal pattern for particles between .1 and 1.3 μm remained flat and could not be related to the diurnal traffic or power demand pattern. The lack of an afternoon peak for particles between .1 to 1.3 μm in the summer diurnal patterns, when photochemical activity would be maximal, suggests that photochemically generated aerosols in the .1 to 1.3 μm range are a relatively small fraction of the total aerosol in New York City. However, the possibility exists that photochemical aerosols are being generated further downwind from urban New York City due to the summertime meteorological conditions in that area. No significant diurnal variations in submicron sulfate and nitrate concentrations or composition were found which further indicates the absence of a significant fraction of local photo-chemically generated aerosol in New York City. A further review of these data indicated that the size and chemical nature of the sulfate in New York was very similar to the sulfate in rural Illinois.[41]

The third study[42] was conducted in Denver from December 1978 to January 1980. The aerosol samples were collected by two auto-mated dichotomous samplers with a 2.5 μm and a 15 μm cut size. The samplers were located at two sites in a north central urban area of Denver. The samplers were operated continuously from mid-December 1978 through January 1980 with minor interruptions for repair, etc. From December 21, 1978 through June 1979 and from December 1979 through January 1980, the samplers were oper-ated for 12-h durations. Filters were changed at 7 a.m. and 7 p.m. Elements were analyzed using XRF; NO_3^- and $SO_4^=$ were analyzed using ion chromatography; and NH_4^+ was analyzed using an ion selective electrode.

The mass concentrations were, in general, equally divided between the two size ranges. However, a higher coarse fraction mass was observed for the daytime sampling at one site near several heavily traveled roadways. The absolute concentrations for all species were generally higher for the nighttime samples, but the percentage contributions were generally lower. This means that the proportion of total mass not identified by XRF was greater for samples collected at night. This did not, however, hold true for K and NO_3^-.

A bivariate correlation analysis was conducted for all major PM components reported in the study. The correlation coefficients were greater than 0.8 when correlated with total mass. Of all the components, K had the highest correlation. Daytime and nighttime correlation coefficients for K versus mass were 0.89 and 0.95 respectively. A further analysis of K with respect to wood burning indicated that a strong correlation existed with the occurrence of secondary usage of wood fires for home heating during the nighttime hours.

The average nighttime fine particulate concentration for NO_3^- was 1.4 times more than daytime samples. Also, the nighttime peak concentrations were more than 2 times greater than those during the daytime. This diurnal variation may have been caused by a number of factors. There may have been lower ammonia concentrations to neutralize nitric acid during the day; ammonium nitrate may have been more volatile and thus not collected; increased sulfuric acid concentration may have reacted with collected ammonium nitrate releasing nitric acid; or the total amount of NO_3^- may actually have been lower. Additional analysis is needed to provide further insight into this apparent diurnal variability of NO_3^-.

The fourth study[43] analyzed diurnal patterns for IP, fine particles (fine), coarse particles (coarse), PM, and eight elements for two sites in the RAMS network in St. Louis, Missouri. The only element that showed a pronounced diurnal pattern was Pb. It demonstrated a distinct afternoon minimum. This pattern seems

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to be unusual because one would expect the noon to 6 p.m. traffic levels to be as great as the 12 a.m. to 6 a.m. and the 6 p.m. to 12 a.m. Another observation in this study was that since elements like Al, Si, Ca, and the coarse fraction did not exhibit diurnal patterns like Pb (an automotive tracer), fugitive dust sources may not necessarily have the impact that other studies have suggested. However, no data were presented regarding the diurnal pattern of Br (also an automotive tracer). If Br did not have a strong diurnal pattern, then possibly the Pb levels may have been influenced by other than traffic-related sources.

In the fifth study,[44] diurnal concentrations of 20 trace elements were measured over a 24-h period in a rural area. The particle size distributions of the elements were determined by an Anderson cascade impactor which separates particles from 8 to 0.1 μm radii. The rural sampling was conducted 5 km west of Niles, Michigan, and 15 km north of South Bend, Indiana. Samples were taken August 21 and 22, 1969 while the entire North Central and Northeastern U.S. were under the influence of a Canadian high pressure system. Large variations occurred in the concentrations of several elements during a 24-h period. Al, Ti, and Mg behaved very similarly; their concentrations varied by up to a factor of 10. However, elements such as Na, K, Fe, Co, and Cr had a variability of about 2.5. The behavior of Mn was between these two extremes.

Pollutants such as sulfur dioxide (SO_2), nitrogen dioxide (NO_2), and carbon monoxide (CO) have shown consistent diurnal patterns with average variations within a factor of 3. Since most of the analyses for these pollutants have been conducted for urban areas, the variation in concentration has been explained by the variation in local source emissions and city ventilation. However, the Michigan-Indiana study[44] was conducted in a rural area where measurements were affected more by distant sources and diurnal meteorological variations.

The Michigan-Indiana study[44] presented some tentative explanations for the variations in the trace elements. PM released

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during nocturnal temperature inversion conditions tends to stay aloft until after sunrise. Daylight hours bring heating and the generation of turbulence that builds upward until the PM layer is reached. Eddy transport to the surface causes a steep morning peak. The maximum mixing level continues to increase until midafternoon, thereby diluting the concentrations. By late afternoon or early evening, the mixing level is usually lower and the thermal stability is higher; thus the concentration is gradually increased. By evening, the concentrations are usually expected to decrease slightly. In most of the cases, however, in the Michigan-Indiana study,[44] the concentrations dropped rapidly during the morning hours, after reaching the lowest levels in the entire sampling period. The explanation was that local ground fog and high relative humidity caused droplet nucleation, followed by sedimentation and/or impaction of enlarged droplets. This was somewhat confirmed by analyzing elements showing the largest variation and by having an early morning minimum with a predominance of larger particles. Although Al, V, Ti, and Mg fell into this category, Na, K, Cr, Co, and Mn had smaller diurnal variations and their concentrations were more uniformly distributed over the 0.1 to 10 μm size range.[44]

Although certain elements seemed to be affected by broad, areawide influences, Br showed a diurnal variation that suggested influences from local sources. Traffic patterns near the monitoring site seemed to closely follow the variation in Br concentration and to verify local influences.

The sixth study, in July and August of 1977 on the summit of Allegheny Mountain in southwestern Pennsylvania,[45] indicated that although the 12-h average $SO_4^=$ levels fluctuated greatly (1 to 25 μg/m^3), the PM unassociated with $SO_4^=$ was relatively constant (about 15 μg/m^3). Table 16 summarizes the ratios for night-to-day concentrations for the major elements in this study.[45]

The seventh study[40] compared 12-h daylight TSP samples with samples collected from 6 p.m. to 6 a.m. in New York City. "Three organic fractions--nonpolar, moderately polar, and polar (acetone

TABLE 16. DIURNAL VARIATIONS FOR DATA FROM ALLEGHENY MOUNTAIN
JULY - AUGUST 1977[45]

Component	Night/Day
Na	0.80
Mg	0.90
Al	0.90
Si	0.95
S	1.00
K	0.90
Ca	1.00
Ti	0.90
V	0.90
Mn	0.80
Fe	0.80
Zn	0.70
Br	0.70
Ba	1.10
Pb	1.00

soluble)--examined. Only the nonpolar (benzene-soluble) fraction showed a significant difference from night versus day."[40] In general, nonpolar organics are primary in origin. These results suggest a local rather than a transported origin for nonpolar POM.

4.5.2 Seasonal Influences

Five studies included in this analysis presented data on seasonal variability.[40,43,46,47,48] In some cases particle size and chemical composition data were both considered in the analysis of seasonal variability and in other cases only the chemical composition was considered.

The first study[40] evaluated the seasonal differences of organic compounds in New York City. Table 17 summarizes the summer-winter comparisons of POM. The summer-winter differences should be largely due to space heating.

The second study[43] was conducted in St. Louis using 1976 data. The data were grouped according to 3 site classifications--urban, suburban, and rural. In general, the urban concentrations for TSP, IP, coarse, and fine particles were higher than suburban concentrations, which were higher than rural concentrations. Concentrations for TSP, IP, coarse, and fine tended to peak during the summer (June through September). "The summer peak was strong for fine, moderately strong for IP, moderate for coarse, and very weak for TSP."[43] Figure 10 presents the TSP seasonal variability for eight elements. The site classification differences are predominant in Figure 10. The spatial differences are pronounced for Pb, V, Ti, and Fe and somewhat less pronounced for S. The S peak is similar to that for fine. The Si, Al, and Ca peaks are similar to those for coarse. The V winter peak reflects the increased use of fuel oil for space heating. The Pb does not appear to have a significant seasonal pattern.[43]

The third study[46] was conducted in Portland, Oregon to identify the major aerosol sources and to quantitatively determine their contributions to TSP levels. A review of the results for

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TABLE 17. SUMMER-WINTER COMPARISONS OF POM IN NEW YORK CITY[a40]

| Year | Fraction | Dispersion-Normalized Concentrations ($\mu g/m^3$) | | |
		Summer[b]	Winter[b]	Difference
1969[c]	Nonpolar	3.6	8.3	4.7
	Polar	3.4	7.6	4.2
	Total	7.0	15.9	8.9
1977[d]	Nonpolar	1.4	6.7	5.3
	Polar	1.5	8.1	6.6
	Total	2.9	14.8	11.8

[a]Weekly samples.

[b]July-August 1969 and 1977; January-February 1969; December 1977; January-February 1978.

[c]TSP samples.

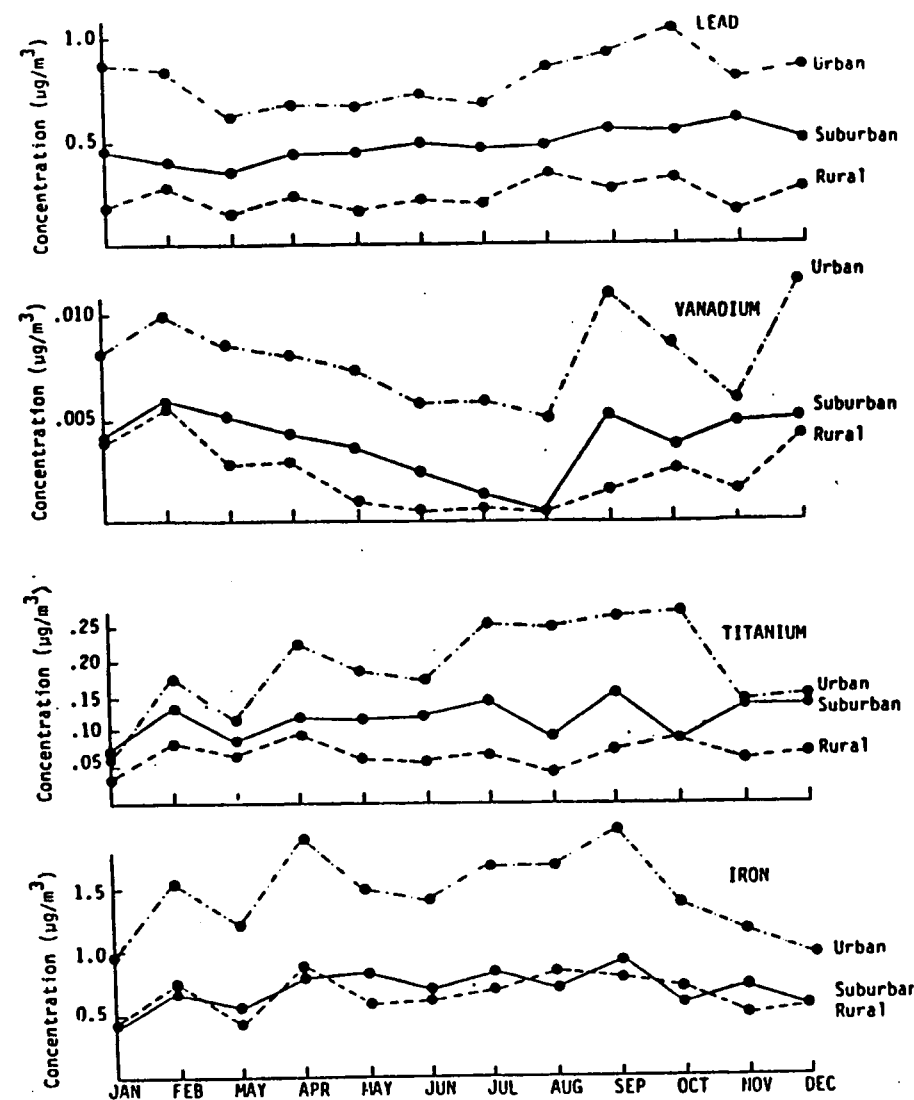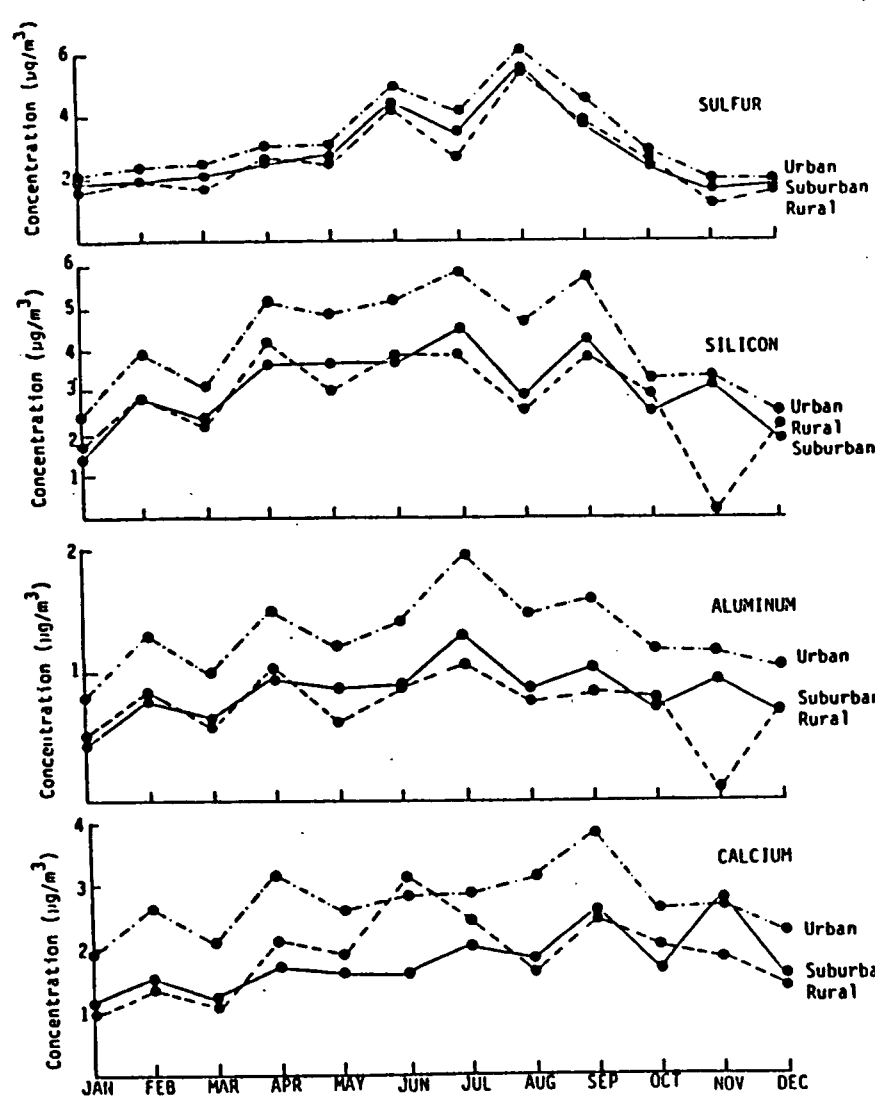[d]Respirable suspended particulate matter samples.

Figure 10. Seasonal patterns of TSP elemental concentrations.[43]

the worst case day for each season indicates that the major
sources contributing to TSP on the worst-case days are not sig-
nificantly different in general from the sources that affect the
annual averages. The major source responsible for seasonal
worst-case days is the geological source category.[46]

The fourth study[47] was conducted in New York City by the New
York University Medical Center to obtain a better understanding
of the type and concentrations of organic compounds in New York
City. Samples were collected during the summer of 1976 and the
winter of 1977. Twenty-four hour TSP samples were collected
during two alternate weeks in August 1976. The samples were
sequentially extracted with three organic solvents and the atmos-
pheric concentrations of the extractable compounds were determined.
The total amount of solvent extractable material (acetone, dichloro-
methane, cyclohexane) for the summer, 1976 is very close to the
yearly average reported for 1968 and 1969. The concentrations of
dichloromethane and acetone extractable compounds significantly
correlated with lead, zinc, and cadmium. Cyclohexane extractable
compounds, however, were not significantly correlated with lead,
zinc, or cadmium.[47]

Data were also collected for three weeks in February, 1977.
The concentrations for the cyclohexane extractables and acetone
extractables were both higher for the winter than for the summer.
The average concentration for dichloromethane extractables were
slightly lower but not significantly different than the summer
values. While the TSP values in New York City have decreased, the
levels of organic compounds do not seem to have changed signifi-
cantly. This seasonal difference suggests that space heating may
be a significant source of organic PM during the winter months.[47]

The fifth study[48] was conducted near Tuscon, Arizona in
January, 1974 to characterize the chemical composition of PM in
the greater Tuscon area. The study included 11 monitoring sites
in and around Tuscon. These sites included 8 urban, 2 near urban
and 1 rural or background. The sampling was conducted every
sixth day with 24-h samples being collected and analyzed using

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atomic absorption. In addition to characterizing the PM, some analyses were conducted with respect to determining the effects of meteorological or seasonal variability on the chemical nature of the PM. The results of these analyses indicate that while it was possible to observe some effects of various meteorological variables upon the PM composition, and concentration, these relationships proved to be weak and more complex than the relationship between the chemical components themselves. However, while the meteorological effects were not straightforward, it was possible to qualitatively assess the influences of local meteorology or climatology. Nonsoil PM components showed a tendency toward winter maximums and summer minimums. Soil components showed maximums in the spring and summer and minimums in the fall. Local climatology may be partially responsible for these apparent seasonal variations. Tucson's climate is typical of a desert: mild winters, hot summers, and low annual precipitation. Summer daytime heating produces intense vertical and horizontal mixing which increases the injection and residence time of large soil type particles. Those components on the other hand that are independent of atmospheric turbulence are rapidly mixed and diluted and therefore, have relatively lower concentrations during these situations.

The desert winters are characterized by intense nighttime radiational cooling. This results in very shallow and stable inversions. Large soil particles under these conditions are removed by sedimentation and therefore have lower concentrations. However, the smaller particles, generally not soil related, are not significantly affected by sedimentation. Therefore, those components in the smaller size ranges are predicted to have higher concentrations in the winter than in the summer.[48]

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SECTION 5.0

RESULTS AND CONCLUSIONS

Sections 3.0 and 4.0 discussed data on the particle size distribution and on chemical composition of PM across the country and provided insights into the nature and the extent of the PM problem. Section 4.0 also presented limited data on the particle sizes of various PM chemical components.

This section compares the results of a combined analysis that considers particle size, chemical composition, site classification and geographic area with the results of other studies not included in this analysis. This section also discusses the nature and extent of the PM across the country and provides additional insight into the hypotheses proposed in Section 1.0.

5.1 TYPICAL PM COMPOSITION BY SITE/GEOGRAPHIC AREA

With the exception of the data in Table 15, the particle size and chemical composition data were considered separately. Also, site classification and geographic area data were considered only in terms of the particle size analysis. Therefore, there was a need to combine the data on particle size and chemical composition with the data on site classification and geographic area to provide a comprehensive assessment of the data in the studies included in this analysis.

Tables 18-22 summarize the chemical composition and particle size data by site classification and geographic area. Table 18 is a summary for urban-commercial sites; Table 19, for urban-industrial sites; Table 20, for suburban-commercial sites; Table 21, for suburban-residential sites; and Table 22, for rural-background sites. Data were not available for all geographic areas within each site classification. The urban-commercial

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TABLE 18. CHEMICAL CHARACTERIZATION OF URBAN-COMMERCIAL SITES BY PARTICLE SIZE

Component	Northwest Conc. at D_{50}, μg/m³			West Coast Conc. at D_{50}, μg/m³			Great Plains Conc. at D_{50}, μg/m³			Midwest Conc. at D_{50}, μg/m³			Southeast Conc. at D_{50}, μg/m³			Northeast Conc. at D_{50}, μg/m³			Southwest Conc. at D_{50}, μg/m³		
	≤2.5 μm	>2.5 μm	≤30 μm	≤2.5 μm	>2.5 μm	≤30 μm	≤2.5 μm	>2.5 μm	≤30 μm	≤2.5 μm	>2.5 μm	≤30 μm	≤2.5 μm	>2.5 μm	≤30 μm	≤2.5 μm	>2.5 μm	≤30 μm	≤2.5 μm	>2.5 μm	≤30 μm
SO_4^-		3.800	4.163									2.850									6.900
NO_3^-		4.200	2.834			0.117												2.600			3.450
NH_4^+																		0.560			1.850
AL	0.210	0.838	2.608	0.050	0.331	0.916	1.983	8.678	2.951	0.262	1.110	2.393				0.089	0.741	1.780	0.700		5.725
Si	0.089	2.204	8.078	0.188	0.995	2.221	0.706	6.152	6.452	0.562	2.616	6.456				0.310	1.910	5.210	0.800		16.125
S	1.395	0.892	1.548	1.612	0.240	1.846	7.637	1.080	4.818	3.774	0.345	8.405				4.316	0.427	7.230	2.240		3.560
Cl	0.478	1.010	1.725	0.072	0.719	1.500	0.145	0.180	0.325	0.144	0.232	0.248				0.171	0.416	0.438			
K	0.153	0.845	0.543	1.000	0.179	0.499	0.300	0.762	1.062	0.097	0.279	0.383				0.205	0.175	0.423	0.100		1.850
Ca	0.067	0.683	1.423	0.099	0.442	1.030	0.410	5.060	3.476	0.093	0.831	1.508				0.263	1.044	1.131	0.080		3.135
Ti	0.018	0.083	0.272	0.010	0.042	0.077	0.568	1.037	0.639	0.011	0.081	0.143				0.013	0.051	0.083	0.010		0.250
V	0.029	0.019	0.224	0.005	0.003	0.011	0.023	0.029	0.115	0.002	0.002	0.004				0.134	0.046	0.361	0.003		0.014
Cr	0.014	0.009	0.031	0.004	0.003	0.015	0.018	0.022		0.002	0.002	0.004				0.027	0.009	0.019			0.004
Mn	0.027	0.031	0.078	0.005	0.006	0.065	0.040	0.033		0.007	0.012	0.018				0.036	0.029	0.048	0.005		0.032
Fe	0.187	0.623	2.215	0.124	0.360	1.354	0.337	2.901	2.105	0.163	0.625	1.076				0.298	0.824	1.330	0.110		2.150
Ni			0.034															0.070			0.006
Cu	0.062	0.029	0.103	0.012	0.006	0.163	0.059	0.016	0.075	0.025	0.029	0.055				0.049	0.019	0.049			0.190
Zn	0.061	0.045	0.143	0.045	0.016	0.100	0.249	0.137	0.386	0.030	0.020	0.071				0.261	0.062	0.381	0.060		0.150
As			0.004									0.260						0.006			
Se			0.006									0.009						0.002			
Br	0.288	0.074	0.345	0.138	0.032	0.352	0.273	0.106	0.378	0.133	0.033	0.199				0.241	0.045	0.248	0.490		0.530
Sr	0.003	0.007	0.010	0.001	0.003		0.010	0.014		0.001	0.002					0.002	0.004	0.006			0.020
Ba			0.092						0.024									0.027	0.074		1.480
Pb	0.866	0.337	0.835	0.614	0.092	1.379	1.517	0.422	1.125	0.623	0.134	0.192				1.001	0.170	1.386	1.680		1.415

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TABLE 19. CHEMICAL CHARACTERIZATION OF URBAN-INDUSTRIAL SITES BY PARTICLE SIZE

Component	Northwest Conc. at D_{50}, μg/m³			West Coast Conc. at D_{50}, μg/m³			Great Plains Conc. at D_{50}, μg/m³			Midwest Conc. at D_{50}, μg/m³			Southeast Conc. at D_{50}, μg/m³			Northeast Conc. at D_{50}, μg/m³			Southwest Conc. at D_{50}, μg/m³		
	≤2.5 μm	>2.5 μm	≤30 μm	≤2.5 μm	>2.5 μm	≤30 μm	≤2.5 μm	>2.5 μm	≤30 μm	≤2.5 μm	>2.5 μm	≤30 μm	≤2.5 μm	>2.5 μm	≤30 μm	≤2.5 μm	>2.5 μm	≤30 μm	≤2.5 μm	>2.5 μm	≤30 μm
SO_4^-			2.409															12.340			
NO_3^-			3.689			0.170												2.013			
NH_4^+																		4.644			
AL			3.881			1.137												1.531			
SI			12.074			3.751												6.796			
S			1.750			3.084												5.696			
Cl			1.719			0.097												0.449			
K			0.697			0.913												0.698			
Ca			2.120			1.063												2.927			
Ti			0.367			0.242															
V			0.030			0.043												0.016			
Cr			0.066															0.203			
Mn			0.168			0.049												0.083			
Fe			4.438			2.009												3.042			
Ni			0.042															0.012			
Cu			0.102			0.020															
Zn			0.265			0.190												0.135			
As			0.005																		
Se			0.010																		
Br			0.309			0.217												0.988			
Sr																					
Ba			0.072																		
Pb			0.986			1.407												0.869			

TABLE 20. CHEMICAL CHARACTERIZATION OF SUBURBAN-COMMERCIAL SITES BY PARTICLE SIZE

Component	Northwest Conc. at D_{50}, $\mu g/m^3$			West Coast Conc. at D_{50}, $\mu g/m^3$			Great Plains Conc. at D_{50}, $\mu g/m^3$			Midwest Conc. at D_{50}, $\mu g/m^3$			Southeast Conc. at D_{50}, $\mu g/m^3$			Northeast Conc. at D_{50}, $\mu g/m^3$			Southwest Conc. at D_{50}, $\mu g/m^3$		
	≤ 2.5 μm	>2.5 μm	≤ 30 μm	≤ 2.5 μm	>2.5 μm	≤ 30 μm	≤ 2.5 μm	>2.5 μm	≤ 30 μm	≤ 2.5 μm	>2.5 μm	≤ 30 μm	≤ 2.5 μm	>2.5 μm	≤ 30 μm	≤ 2.5 μm	>2.5 μm	≤ 30 μm	≤ 2.5 μm	>2.5 μm	≤ 30 μm
$SO_4^=$	50.000																	11.999		1.045	51.050
NO_3^-	1.940					0.093												1.464		0.439	2.381
NH_4^+	1.945																	3.812			1.946
AL	0.156					1.802												1.347		2.668	2.824
Si	0.376					4.576												6.322		8.581	8.957
S						3.052												5.500			
Cl						0.435												1.066			
K	0.124					0.947												0.636		1.192	1.315
Ca	0.107					1.821												3.090		1.065	1.172
Ti	0.006					0.231														0.216	0.221
V						0.030												0.294			
Cr						0.022												0.003			
Mn						0.059												0.065			
Fe	0.103					2.426												2.410		1.283	1.426
Ni						0.033												0.010			
Cu						0.020														0.047	
Zn	0.051					0.151												0.179			0.098
As																					
Se																		0.004			
Br	0.628					0.327												0.821		0.163	0.791
Sr																					
Ba																					
Pb	1.758					1.600												0.666		0.542	2.300

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TABLE 21. CHEMICAL CHARACTERIZATION OF SUBURBAN-RESIDENTIAL SITES BY PARTICLE SIZE

Component	Northwest Conc. at D_{50}, µg/m³			West Coast Conc. at D_{50}, µg/m³			Great Plains Conc. at D_{50}, µg/m³			Midwest Conc. at D_{50}, µg/m³			Southeast Conc. at D_{50}, µg/m³			Northeast Conc. at D_{50}, µg/m³			Southwest Conc. at D_{50}, µg/m³		
	≤ 2.5 µm	>2.5 µm	≤ 30 µm	≤ 2.5 µm	>2.5 µm	≤ 30 µm	≤ 2.5 µm	>2.5 µm	≤ 30 µm	≤ 2.5 µm	>2.5 µm	≤ 30 µm	≤ 2.5 µm	>2.5 µm	≤ 30 µm	≤ 2.5 µm	>2.5 µm	≤ 30 µm	≤ 2.5 µm	>2.5 µm	≤ 30 µm
SO₄⁼			5.066			0.087															
NO₃⁻			0.007																		
NH₄⁺																					
AL						1.965			0.833									0.863			
SI						2.868			3.033												
S						2.298			2.733												
CL						0.900												1.570			
K						0.738															
Ca						0.762			1.767												
TI						0.048			0.117												
V						0.026			0.004									0.320			
Cr						0.013															
Mn			0.053			0.027												0.022			
Fe			0.960			1.297			0.700									0.777			
Ni						0.013															
Cu						0.063															
Zn			0.127			0.080												0.128			
As			0.007																		
Se																		0.003			
Br						0.174															
Sr																		0.152			
Ba																					
Pb			0.293			0.679			0.473												

TABLE 22.   CHEMICAL CHARACTERIZATION OF RURAL-BACKGROUND SITES BY PARTICLE SIZE

Component	Northwest Conc. at D_{50}, $\mu g/m^3$			West Coast Conc. at D_{50}, $\mu g/m^3$			Great Plains Conc. at D_{50}, $\mu g/m^3$			Midwest Conc. at D_{50}, $\mu g/m^3$			Southeast Conc. at D_{50}, $\mu g/m^3$			Northeast Conc. at D_{50}, $\mu g/m^3$			Southwest Conc. at D_{50}, $\mu g/m^3$		
	≤ 2.5 μm	>2.5 μm	≤ 30 μm	≤ 2.5 μm	>2.5 μm	≤ 30 μm	≤ 2.5 μm	>2.5 μm	≤ 30 μm	≤ 2.5 μm	>2.5 μm	≤ 30 μm	≤ 2.5 μm	>2.5 μm	≤ 30 μm	≤ 2.5 μm	>2.5 μm	≤ 30 μm	≤ 2.5 μm	>2.5 μm	≤ 30 μm
$SO_4^=$			3.392															8.306			
NO_3^-			2.266															0.600			
NH_4^+																		2.534			
Al			1.720						0.750				0.020	0.195	0.215			0.869			
Si			4.936				0.500	4.000	3.233				0.038	0.580	0.618			2.801			
S			0.741				12.600	0.900	6.133				3.700	0.204	3.948			2.445			
Cl			0.785										0.010	0.007	0.017			0.102			
K			0.404				0.300	0.900	1.200				0.040	0.108	0.148			0.132			
Ca			0.700				0.500	4.200	2.533				0.016	0.322	0.338			0.398			
Ti			0.118				0.100	0.200	0.133				0.002	0.018	0.020			0.040			
V			0.015						0.002					0.002	0.002			0.005			
Cr			0.015															0.001			
Mn			0.032															0.012			
Fe			0.900				0.300	1.300	0.867				0.028	0.118	0.146			0.383			
Ni			0.009										0.001	0.001	0.002			0.007			
Cu			0.089										0.003	0.005	0.008						
Zn			0.105				0.130	0.150	0.280				0.009	0.004	0.013			0.021			
As			0.035										0.002	0.001	0.003						
Se			0.001										0.041	0.001	0.002			0.003			
Br			0.070				0.060	0.040	0.100					0.005	0.023			0.145			
Sr													0 018								
Ba																		0.004			
Pb			0.202				0.510	0.110	0.340				0.097	0.014	0.111			0.163			0.395

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site summary (Table 18) had data for all geographic areas except the SE. The urban-industrial site summary (Table 19) had limited data (i.e., $\leq$30 μm only) for only three geographic areas (NW, W, and NE). The suburban-commercial site summary (Table 20) had some limited data for the NW, W, NE, and SW. The suburban-residential site summary (Table 21) had very limited data for the NW, W, GP, and NE. The rural-background site summary (Table 22) had slightly more data than the other summaries for some particle sizes but only for the NW, GP, SE, and NE.

According to Table 18, very little $SO_4^=$ and NO_3^- data are available for urban-commercial sites. However, S concentration data were available which provide some insight with respect to the $SO_4^=$ concentrations. The S data indicates that the highest concentrations occur in the GP, MW, and NE. The concentrations for these geographic areas range from 4 to 8 μg/m^3. The S concentrations for the other geographic areas range from 1 to 2 μg/m^3. Although the highest S concentrations occur for particles $\leq$30 μm, S has its greatest impact in terms of the overall concentration for particles $\leq$2.5 μm. However, a large fraction of S would still be found in particles $\geq$ 2.5 μm. Therefore, sulfur and sulfur-related components such as $SO_4^=$ have dominant influences on the overall PM concentration in all areas with the greatest impact occurring in the GP, MW, and NE where there are significant amounts of coal and oil combustion and a possible long-range transport component.

Data from the New York Summer Aerosol study of 1976[41] provide some conclusions regarding $SO_4^=$. The first conclusion is that approximately 25% of the TSP in New York City is sulfate. The second is that an average of 35% of the TSP and about 75% of the sulfate is at times associated with long-range transport processes. The third is that long-range transport is a major influence on the $SO_4^=$ and TSP levels in New York City.

The concentrations of crustal elements such as AL, Si, and Mn are relatively uniform throughout the United States, except in the SW. The crustal element concentrations are generally the

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highest in terms of both the absolute concentration and the overall percent contribution for particles $\leq$30 μm. The impacts of these elements are significantly less for particles $\leq$2.5 μm where fuel combustion sources and secondary aerosols dominate. Crustal element data in the SW indicate that the concentrations in many cases are almost twice the concentrations for these elements in all other geographic areas. These data support previous studies that have indicated that fugitive dust or soil-related particles have significant impacts on the PM concentrations in the SW.[49,50]

The Pb and Br data in Table 18 indicate that these concentrations are consistent from area to area. The Br data indicate little difference in absolute concentrations (.1 to .3 μg/m^3) for particles $\leq$2.5 and $\leq$30 μm. The Pb data also indicate in many cases little difference in the absolute concentration (.6 to 1.5 μg/m^3) for particles $\leq$2.5 and $\leq$30 μm. In general, the absolute Pb concentration and the percent contribution to the overall PM concentration is higher for particles $\leq$2.5 μm than for particles $\leq$30 μm.

In conclusion, urban site concentrations appear to be influenced by four major sources: fuel combustion, process sources, soil or fugitive dust-related sources, and motor vehicles. For particles $\leq$2.5 μm, the dominant sources appear to be fuel combustion evidenced by the significant contribution of S and S-related compounds and motor vehicles evidenced by the Pb and Br levels. For particles $\leq$30 μm, the major influences to the total mass appear to be fugitive dust sources evidenced by the significant contribution of crustal elements; fuel combustion and process sources evidenced by the S, Fe and in some cases, NO_3^- levels; and motor vehicles evidenced by the relatively significant concentrations of Pb and Br.

According to Tables 19 through 21, the data available for review are limited. For urban-industrial sites, no data are available for particles $\leq$2.5 μm. Additionally, no data are available for the GP, MW, SE, and SW. The data that are available

indicate a significant contribution of $SO_4^=$ especially in the NE. As with the urban sites, the crustal elements appear to dominate the overall PM concentrations for particles ≤ 30 μm.

Data for the suburban-commercial sites are similar to data for the urban-industrial sites. That is, only the NW has data for particles ≤ 2.5 μm and no data are available for the GP, MW, and SE. The crustal elements appear to influence the suburban-commercial sites more than the urban-commercial and urban-industrial sites.

A review of Table 21 indicates very little data exist for suburban-residential sites. In some cases data are available for only a few components. Because of the limited data, the suburban-residential sites can not be characterized.

Finally a review of Table 22 (rural sites) indicates that in terms of the relative concentrations, all the components had concentrations that were lower than those for the urban or industrial sites. With the exception of the NE, which appears to have significant influences from $SO_4^=$ and NO_3^-, the contributions seem to be evenly split between S and S-related compounds and the crustal elements. The influence of motor vehicles was noticably less as evidenced by the lower Pb and Br concentrations. The limited data for particles ≤ 2.5 μm indicate that S and S-related compounds again have the most significant influence, followed by Pb and in some cases crustal elements.

5.2 COMPARISON WITH PREVIOUS ANALYSES

To date, most studies have attempted to characterize PM for a particular city, region, or geographic area. Very few studies have attempted to provide a nationwide characterization of the PM composition.

One study that did attempt a nationwide characterization was published in 1977 by Faro and McMullen.[51] This study summarized the measurements of 11 metals (Be, Cd, Cr, Co, Cu, Fe, Mn, Hi, Pb, Ti, and V) in TSP samples taken from 1965 through 1974 from the EPA's National Air Surveillance Network of hi-vol air

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monitoring stations. No particle size data were available for this analysis. Ninety-two urban and 16 nonurban sites were included in this analysis. Data were summarized in two ways. First, profiles were prepared showing the distribution of each metal. Second, profiles were prepared to represent the fraction of each metal in the total TSP sample expressed as metal per million parts of collected TSP. These profiles permit a comparison of the metals in TSP with the geological data on the relative abundance of these metals in the earth's surface.

In Figure 11, the width of the concentration profile is proportional to the percentage of stations in each cell. In general there is a contrast between the urban and nonurban sites for 10 of the 11 elements. Cu did not show this contrast, primarily because the Cu concentration (in many cases) is due to contamination attributed to the wearing of the commutator in the hi-vol motor.[52] In the second profile, referred to as the relative abundance profile (Figure 12), the width of the profile is proportional to the percentage of stations in each cell. The solid line or bar denotes the range of the metal's natural abundance as measured in surface soil samples at some 863 sites.[53] The profiles for Pb (Figures 11 and 12) indicate that the concentrations in urban particles are substantially higher than those in the soil surface. The nonurban Pb profile, however, overlays the soil sample range.

Figure 13 presents the concentration profiles for the remaining 10 elements. With the exception of Cu, which has the problem noted above, the urban profiles are consistently shifted toward higher concentrations. Figure 14 presents the relative abundance profiles for the remaining 10 metals. The profiles for Be and Co are dashed lines to signify the tentative nature of the data. A review of Figures 13 and 14 indicates that Fe and possibly Mn and Ni exhibit urban enrichment although not significantly above the soil sample range; V exhibits enrichment for some urban stations, mostly in the NE; and Cd exhibits some general enrichment.
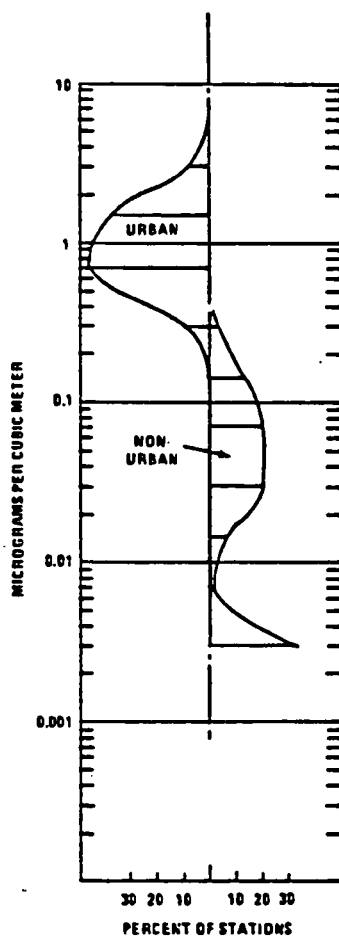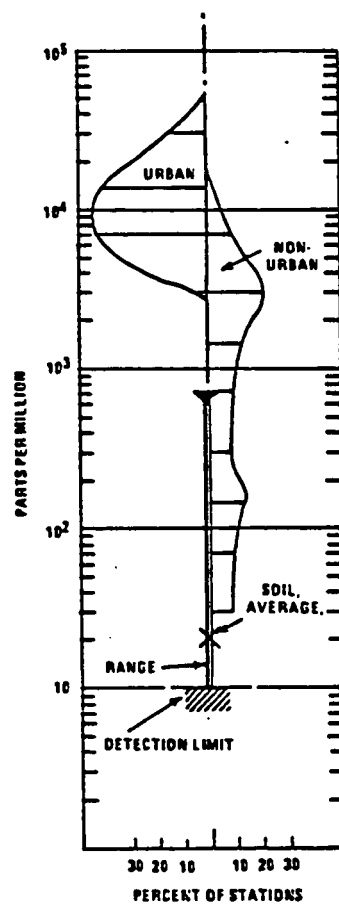
Figure 11. Concentration of lead in air.[48]

Figure 12. Relative abundance of lead in airborne
particulates and in soil samples.[48]

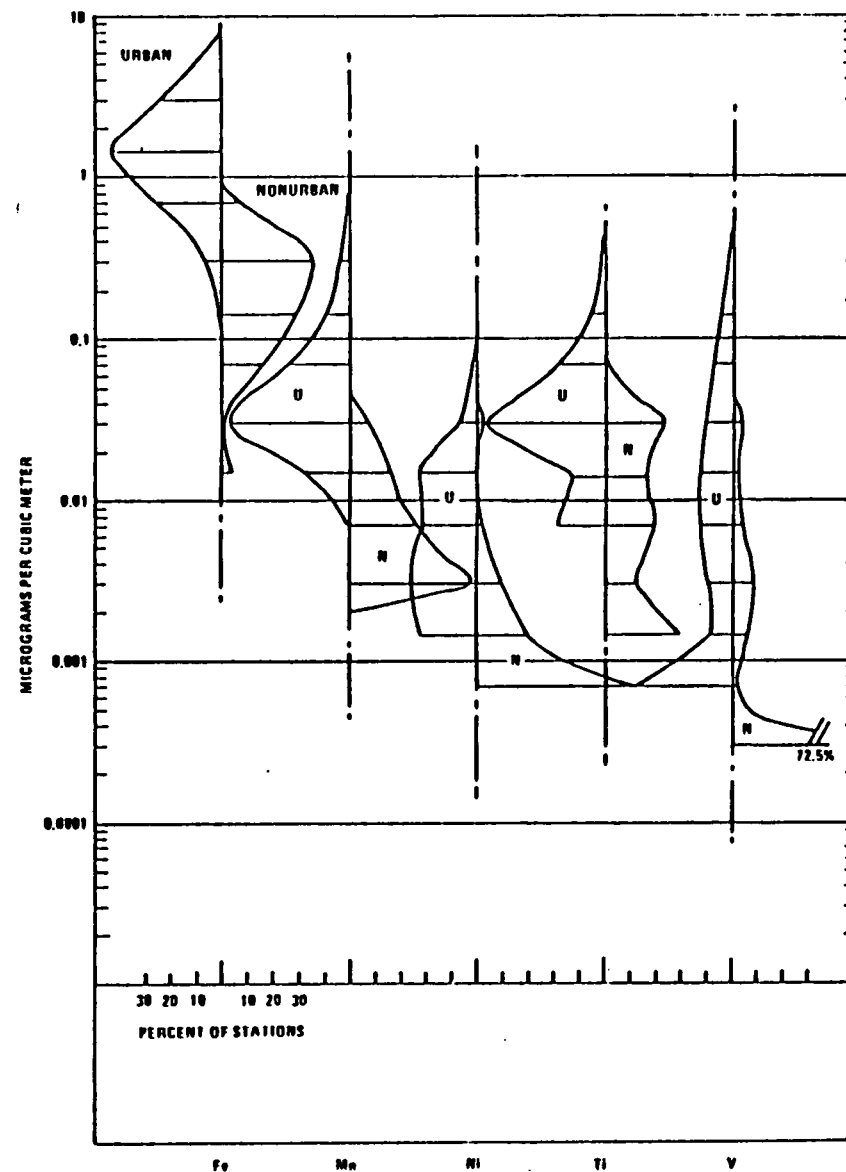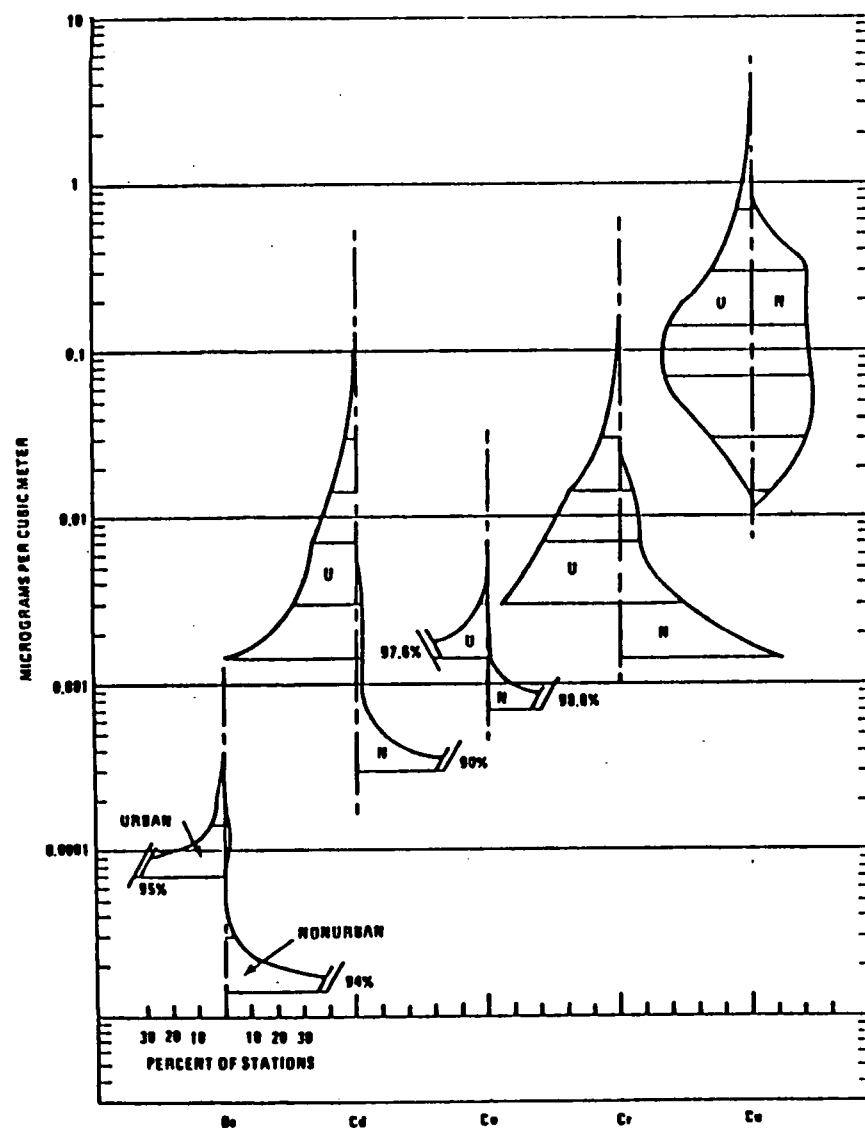(Courtesy of Journal of the Air Pollution Control Association)

Figure 13. Concentrations of particulate metals in air.[48]

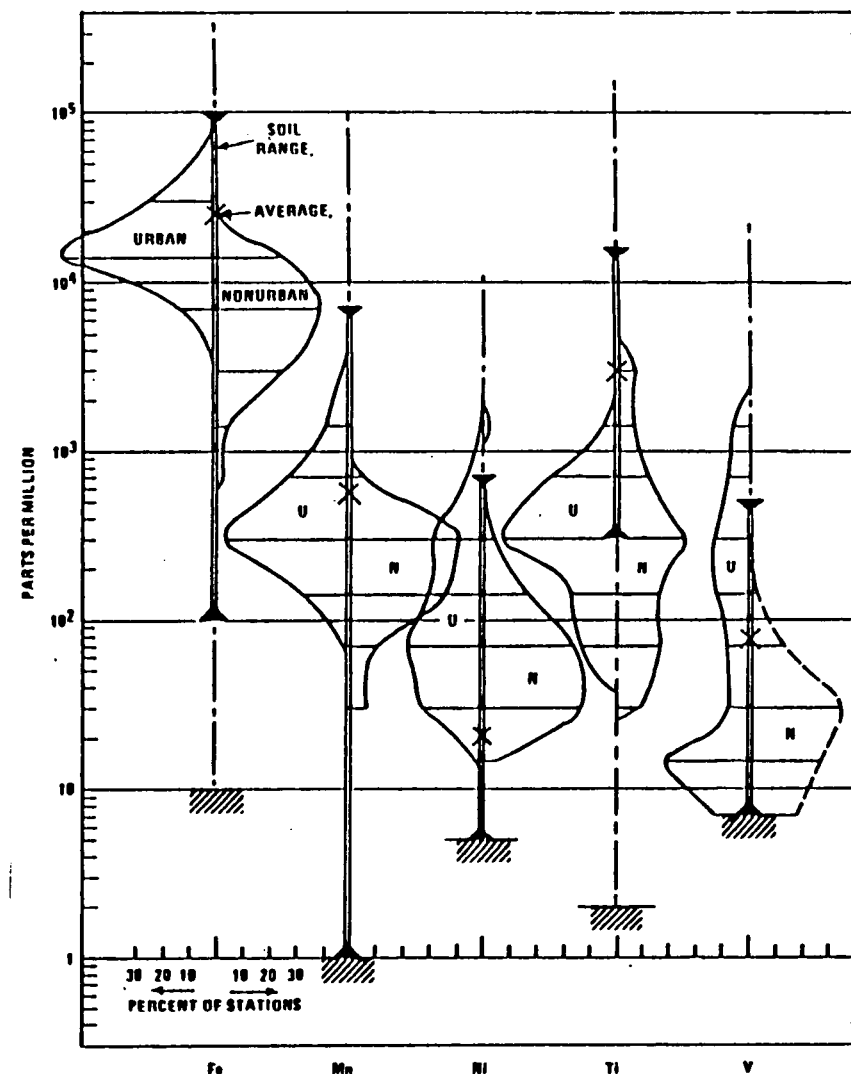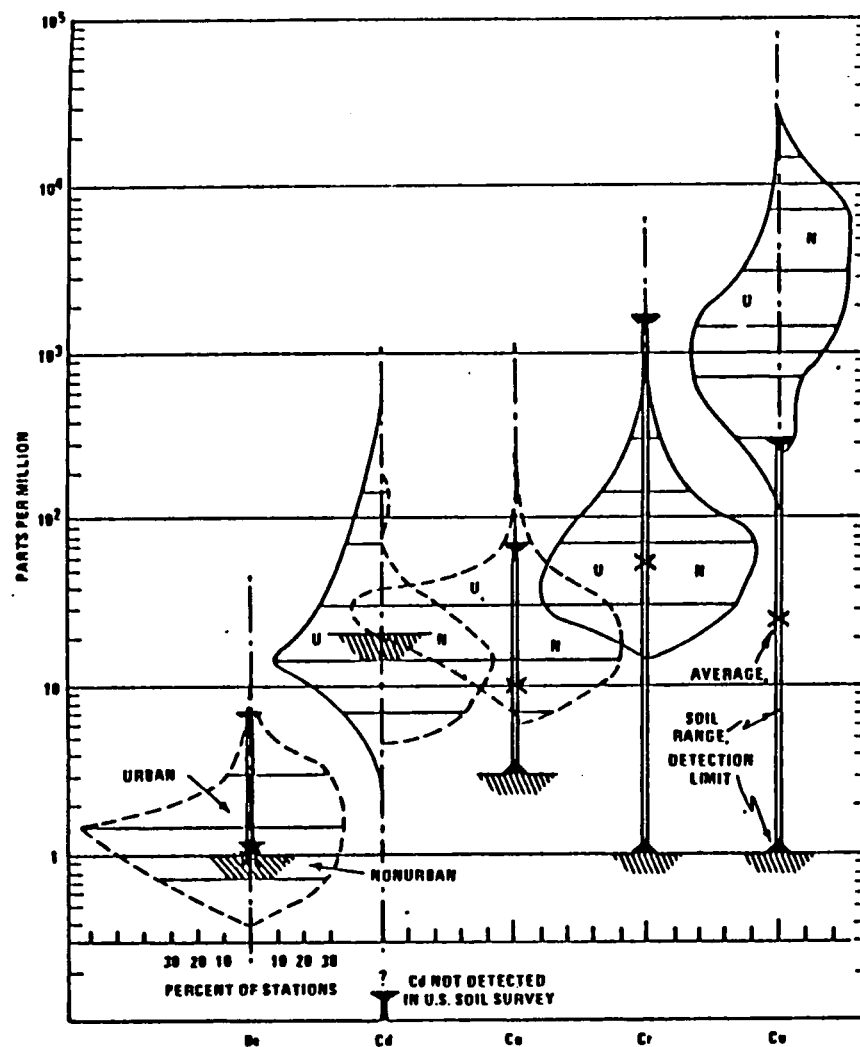(Courtesy of Journal of the Air Pollution Control Association)

Figure 14. Relative abundances of metals in airborne particulates and in soil samples.[48]

(Courtesy of Journal of the Air Pollution Control Association)

Although this study[51] did not contain particle size data or data by geographic area, it seems to support the results presented in Section 5.1 on the chemical nature of the PM across the country. Table 23 presents a summary of the estimated contributions of various sources in a number of cities.[54] The chemical composition of PM depends on the origin of the PM. For example, the elements present in road dust are primarily elements such as aluminum and silicon that are found in the materials used in the road surface and the earth's crust and lead that is emitted in the exhaust of motor vehicles.

The other study that provided limited data on particle size and chemical composition is a preliminary characterization of IP in urban areas.[23] This study compared the IP data from a number of cities across the country, and conducted a detailed review of the data from the Regional Air Pollution Study (RAPS) conducted in St. Louis, Missouri. Figure 15 (pie charts) summarizes the information from the RAPS' data. A review of Figure 15 indicates that $SO_4^=$ dominate the fine fraction ($\leq$2.4 µm), and crustal elements dominate the coarse fraction (2.4-20 µm) at both the urban and nonurban sites. The influence of $SO_4^=$ was slightly greater in nonurban than in urban areas due to urban motor vehicle emissions. Figure 16 contains similar pie charts for the data contained in this analysis. Because the data were limited for suburban and rural sites, the data were combined and designated nonurban for the purpose of constructing Figure 16. The fine fraction are particles $\leq$2.5 µm, and the coarse fraction are particles between 2.5 and 30 µm. Although the data base on which Figure 15 was constructed is limited to one area (St. Louis), it provides additional support and compares favorably with the results presented in Figure 16 on the chemical and physical nature of the PM across the county.

5.3 CONCLUSIONS

The main purpose of this analysis was to provide EPA with information on the PM particle size and composition (including

TABLE 23. ORIGINS OF AMBIENT URBAN AEROSOLS BASED ON CHEMICAL ELEMENT BALANCES[54]

| Source | Estimated Contribution (% of TSP) | | | | | | |
	Washington, D.C.[a] 1976 Total	St. Louis, Mo.[b] 1976 Fine	St. Louis, Mo.[b] 1976 Coarse	Portland, Oreg.[c] 1977/78 Fine	Portland, Oreg.[c] 1977/78 Total	Pasadena, Calif.[d] 1970 Total	Chicago, Ill.[e] 1971 Total
Primary							
Crustal dust	24	9	56	–	–	11.4	18
Urban dust	–	–	–	4.7	46	–	–
Limestone (cement)	4.1	0.8	27	–	–	1.7	3.2
Sea salt	0.9	–	–	2.5	2.1	1.3	–
Coal	6.3	–	–	–	–	–	6.4
Residual oil	0.6	–	–	1.6	0.9	0.1	1.4
Refuse incineration	1.4	–	–	–	–	–	–
Motor vehicles	7.1	8	3	14[f]	7.8[f]	13.5[g]	2.8
Vegetative burning	–	–	–	15	9.3	–	–
Paint pigment	–	0.2	1	–	–	–	–
Steel processing	–	0.4	2	1.5	1.5	–	3.9
Trace elements	–	0.6	1	–	–	–	–
Other industry	–	–	–	1.8	3.8	7.3	–
Nonvolatile carbon	–	–	–	4.1	2.3	4.7	–
Secondary							
NH_4^+	1.4	} 59	6 {	–	–	–	–
SO_4^{2-}	14			10	5.1	>10	11.5
NO_3^-	3.2	–	–	7.5	3.8	~0.1	5.3
Volatile carbon	–	–	–	16	9.4	22	–
Fraction accounted for (%)	63[h]	78	96	79	92	>72.3	53

[a] Kowalczyk (1979).
[b] Dzubay (1979).
[c] Watson (1979).
[d] Friedlander (1973).
[e] Gatz (1975).
[f] Includes only emissions from leaded fuel vehicles. Others presumably are included in volatile and nonvolatile carbon components.
[g] Includes auto exhaust (8.2%), tire dust (0.8%), diesel exhaust (1.8%), and aircraft exhaust (2.7%).
[h] Discrepancy may be rather large because the measured TSP was taken from District of Columbia monitoring data, which included only urban sites, whereas three of the ten stations for the chemical data were rural.
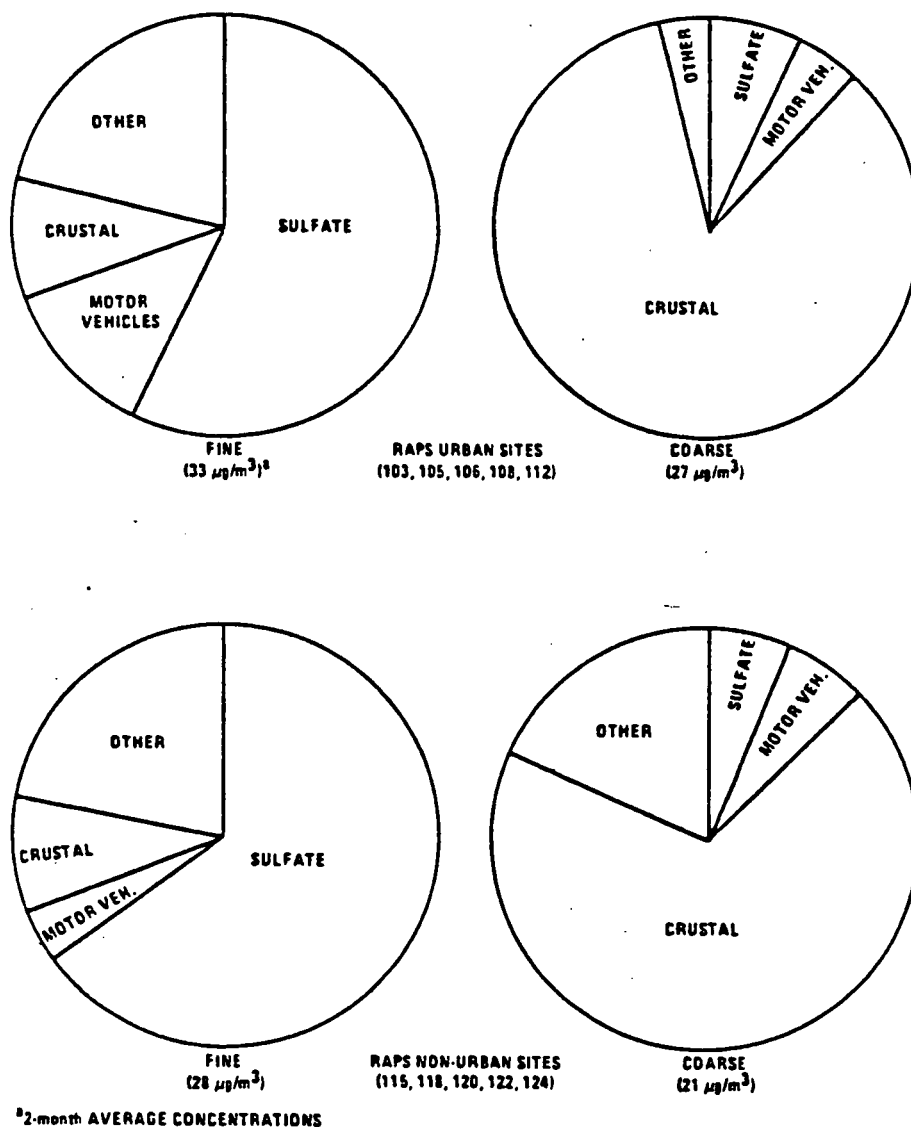
OTHER

CRUSTAL

SULFATE

MOTOR
VEHICLES

OTHER

SULFATE

MOTOR VEH.

CRUSTAL

FINE
(33 μg/m³)ᵃ

RAPS URBAN SITES
(103, 105, 106, 108, 112)

COARSE
(27 μg/m³)

OTHER

CRUSTAL

SULFATE

MOTOR VEH.

OTHER

SULFATE

MOTOR VEH.

CRUSTAL

FINE
(28 μg/m³)

RAPS NON-URBAN SITES
(115, 118, 120, 122, 124)

COARSE
(21 μg/m³)

ᵃ2-month AVERAGE CONCENTRATIONS

Figure 15. Source contribution at RAPS sites.[23]

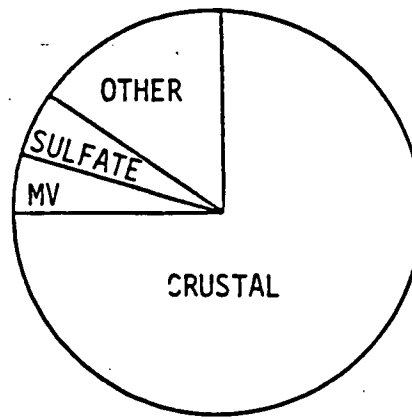(Courtesy of Journal of the Air Pollution Control Association)
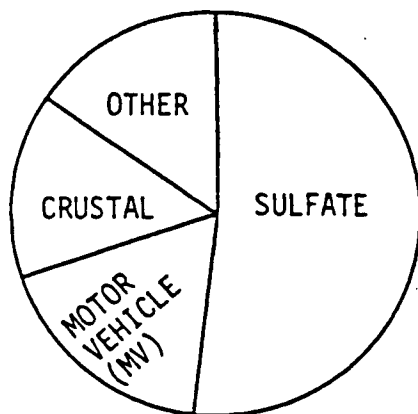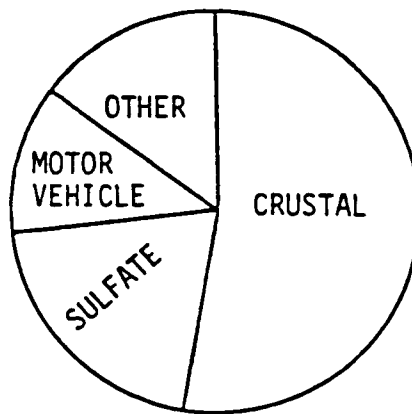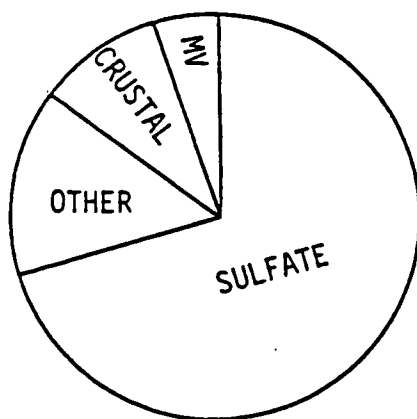
URBAN

NONURBAN

Figure 16. Summary of relative source contributions for sites included in this analysis.

the chemical and physical nature of the particulate). A secondary purpose was to evaluate several hypotheses (Section 1) regarding PM, to the extent possible, based on the data available.

Five conclusions can be drawn regarding this analysis. These conclusions are divided into five main areas: the type of data available; the amount of data available; the particle size of the PM; the chemical composition of the PM, and the response to the hypotheses presented in Section 1.2.

Available data were extremely variable in terms of the methods used to measure (hi-vol, dichotomous samplers, cascade impactors, etc.) and analyze the ambient PM levels. In many of the methods used to collect particle size data the cut sizes of the samplers and the filter media for collecting the samples differed. Many of these samplers have problems with particle bounce; others are sensitive to windspeed and wind direction. It was difficult because of the limited nature of this study to evaluate each study for problems that may have existed in using certain sampling methods or analytical techniques; accordingly all data available from the studies included in this analysis were considered independent of the method used to collect and analyze the data. Therefore, some data used in the analysis may not be directly comparable. The results, however, seem remarkably consistent with other data available from previous studies. Thus, the results can be used to clarify or provide additional insight into the nature and extent of the PM problem across the United States, regardless of the variability in the types of data available. The limited amount of data available for certain particle sizes, geographic areas, and site classifications made it very difficult in some cases to completely characterize the nature and extent of the PM problem. Accordingly, care should be taken in using the absolute values in the summaries of particle size, chemical composition, or both. Absolute values in some cases represent averages for only a few sites. In other cases, although a considerable amount of data may have been available it may have only been for one specific area or site type. Therefore,

the ranges in the summaries should be considered along with the typical or mean concentrations for a more complete understanding of the PM composition in the United States, because of the limited amount of data available in many cases.

The particle size data indicate that, in general, urban sites have the highest concentrations within a particular geographic area for all three particle sizes included in the analysis. Thus, particles ≤ 2.5 μm and ≤ 15 μm generally have the same relative distributions of concentrations in terms of site classifications as particles ≤ 30 μm. A review of the data in terms of geographic area indicates that the NE has highest concentration of particles ≤ 2.5 and ≤ 15 μm and the W, GP, and SW have the highest concentrations in terms of particles ≤ 30 μm. The ratio of the concentration for particles ≤ 15 μm to the particles ≤ 30 μm in terms of geographic distributions varied from 49% to 75%, with an average of 54%. The ratio of the concentrations for particles ≤ 15 μm to the particles ≤ 30 μm in terms of the site classification distribution varied from 36% to 71% with an average of 56%. Some recent work by EPA to analyze the ratio of concentrations for particles ≤ 15 μm to particles ≤ 30 μm indicates that the ratio ranged from .6 to .7.

Chemical composition data are very consistent throughout the United States. Because there were very little data available for suburban and rural sites compared to urban sites, the data from all other site classifications were grouped and considered as nonurban for assessing the overall differences in the chemical composition of particles ≤ 2.5 μm, compared to particles between 2.5 and 30 μm. The analysis of data on particles ≤ 2.5 μm indicates that $SO_4^=$ and motor-vehicle-related components are the dominant influences in both urban and nonurban sites, with the motor-vehicle-related component having a slightly larger urban influence. For particles between 2.5 and 30 μm, the crustal elements are the dominant influence, with additional contribution from $SO_4^=$ and the motor-vehicle-related component especially in the urban areas. The greatest $SO_4^=$ and motor-vehicle-related

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impacts occur at the urban sites in the NE and the greatest
impacts for the crustal elements occur in the urban SW. These
results seem consistent with previous analyses for these geo-
graphic areas.

The results in Sections 3.0 and 4.0 and the conclusions
presented here provide insight to the hypotheses in Section 1.2.
With regard to the first hypothesis, there appears to be a con-
sistent relationship between IP (particles $\leq$15 µm) and TSP
(particles $\leq$30 µm). The ratio of IP to TSP is 50 to 60%, with
values as low as 36% and as high as 75%, depending upon the
geographic area or site type.

The second hypothesis is that over 50% of the fine particu-
late mass is of an anthropogenic origin. Data from California[29]
indicate that 40% of the fine PM comes from primary anthropogenic
sources and 25% comes from secondary anthropogenic sources. Data
from the New York Summer Aerosol Study[41] also indicate that $SO_4^=$
accounts for as much as half of the fine particulate mass concen-
tration. Based on the above data and other data available in
this study, the majority of the fine particulate mass appears to
be anthropogenic in origin. $SO_4^=$, Pb, Br, and secondary aerosols
appear to be the dominant influences on the total mass for
particles $\leq$2.5 µm. Although some PM components (Si, Al, M, etc.)
are found in the soil and the ambient levels may be the results
of natural activities, these elements or components have been
shown to be generally enriched in the urban environment which
would indicate that their air quality levels are in part a result
of man's activity.[51]

The third hypothesis is that the relationship between IP and
TSP can be defined with specific source categories characterized
by emission sources, meteorological characteristics, and site
locations. Little or no information was available on emission
sources and meteorological characteristics; therefore, no in-
sights can be provided regarding the characterization of IP or
TSP with respect to those variables. Some data, however, were
available with respect to the influence of geographic area and

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site location or classification. These data did indicate that
geographic area and site classification do influence the IP and
TSP concentrations. These data are admittedly weak for certain
geographic areas and site classifications. Therefore, additional
data are needed before a thorough characterization can be com-
pleted regarding geographic area and site classification, espec-
ially beyond urban versus nonurban comparisons.

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APPENDIX A

STUDIES LISTED IN REFERENCE 3

Studies conducted	Purpose	Size ranges (μm)	Sampling protocols	Air sheds	Mass and chemical anal.	Source Info	Meteorology
The New York Seasonal Aerosol Studies (NYSAS) 1976–1979[1,2]	Characterization of the ambient aerosol	Continuous distributions; mass fraction in IPM-EPA, FP	Summer and Winter Intensive Campaigns of 4 to 6 weeks in duration 6h, 24h samples	NYC—Metro Area and surrounding rural—suburban	trace elem; ions; organics; mass	no details	local, synoptic
Trace Organics Compounds in NYC 1976–1980[3]	Biologically active organics and sources	0 to 2.5, 0 to 3.5	Continual Weekly Sampling, yearly	NYC and Sterling-Forest, NY	Organics; bacterial mutagenicity and alkalating activity; mass	no details	local
Urban Evaluation of Non-Traditional Sources—Canada 6-25-79 to 9-7-79[4]	Nontraditional source impact	0–2.5; >2.5 to 15	12 h samples	Hamilton, Ontario	trace elem; mass	no details	no details
Allegheny Mountain Experiment 7-24-77 to 8-11-77[5]	Determine the nature of sulfate in the northeast	multistage impactors	12 h samples	Allegheny Mtn PA	trace elem; ions, mass	no details	local
Regional Air Pollution Study (RAPS) 1974–1977[6]	Develop, evaluate regional air quality models	0–2.5, >2.5–25	6h; 12 h samples	100 km region around St. Louis, MO	trace elem; $SO_4^=$, mass	mass and SO_2	synoptic and local
Trace Elements in Urban Aerosols 1974–1980[7]	Receptor models and source allocation	various ranges ≤3.5	Continual weekly low volume sampling, yearly	New York City	trace elem.	mass only	local
Denver Aerosol Study 12-78 to 4-80[8]	Assistance to EPA epidemio study	0 to 2.5; >2.5 to 15	Urban samples	Denver	trace elem; ions; mass	no details	none
Sulfate Regional Experiment (SURE) 7-77 to 10-78[9]	Characterization of $SO_4^=$ in the Northeast U.S.	0–30; 0–12; 0–2.5	All year sampling with periodic intensive campaigns; 24h and 3 h samples	Eastern U.S.	trace elem; carbon; ions	emission inventory SO_2	NWS, dewpoint and temperature
Portland Aerosol Characterization Study (PACS) 7-77 to 3-78[10]	State Implementation Plan	0–30; 0–15; 0–2.5	24h and 8h samples	Portland, OR	trace elem; carbon; ions	emission invent. and source sampling	10 local met stations; upper air winds
Willamette Valley Field and Slash Burning Study Summer 1978[11]	Field and Slash Burning	0–30; 0–2.5; >2.5–15	24 h and 2h samples	Willamette Valley, OR	trace elem. carbon; C^{14}; ions	field and slash burning acreage	surface winds
Denver Winter Haze Study Nov–Dec 1978[12]	determine components of haze	0–30; 0–15; >2.5–15	24h and 4h samples	Denver, CO	Ions; trace elem; carbon	emission inventory	26 local met stations
California Aerosol Characterization Experiment (ACHEX) July–Nov 1972; July–Oct 1973[13]	Characterization of urban aerosols in Calif.	Continuous distributions	24h and 2 h mass samples; 10 min size in situ	14 California cities	Ions; trace elem; carbon	emission inventory	Complete met stations

Studies conducted	Purpose	Size ranges (μm)	Sampling protocols	Air sheds	Mass and chemical anal.	Source Info	Meteorology
Tucson Arizona Study 1974–1975 9-75 to 10-76[14]	Application of multi element receptor models	0–30; 0–2	24 h samples	Tucson, AZ and desert	Ions; trace elem	none	NOAA monitoring
Houston Visibility Study 6-80 to 6-81[15]	Relationship of particle composition and size to visibility	0–2.5; >2.5–15	12h samples every 3rd day	Houston, TX	Ions; trace elements; mass	none	NWS
Intercomparison study of Aerosol Composition Samplers 5-77[16]	Evaluation of Aerosol samplers	0–30 inclusive	12 h samples	Charleston WV	Ions; trace elements; mass	none	local
Montana Health Study 1978–1979[17]	Interlationship of human health and IPM-EPA	0–30; 0–2.5; >2.5–15	24h	5 cities in Montana	Mass only	none	none
Harvard Six Cities Study 1975–1980[18]	Characterization of indoor air ambient. A.P. with Epid. Study	0–30; 0–3.5; 0–2.5; >2.5–15	24h; sixth day, third day; and selected everyday	Portage WA; Topeka, KS; Kingstown, TN; Watertown, MA; St. Louis, MO; Steubenville, OH	SO$_4^-$ trace elem; mass	none	NWS
Community Health and Environmental Surveilance System 1969–1974[19]	National Epid. study in a set of cities	Cascade Impactors and Cyclones	24h	Los Angeles, CA; Salt Lake City, UT; St. Louis, MO; NY; NJ; Chattanooga, TN; Birmingham, AL; Charlotte, NC	Mass; SO$_4^-$	descriptive	unknown
Florida Sulfur Oxide Study 7-76 8-76 12-76[20]	Characterization of particles in Florida	Impactor samples		Pensacola, Miami and other Florida locales	trace elements; mass	none	unknown
Intercomparison Study of Aerosol sampling instruments Summer 1976[21]	Evaluation of Aerosol samples	0–3,5; >3.5	24 h	Charleston WV	trace elements; Ions; carbon nitrogen; mass	none	none

Studies conducted	Purpose	Size ranges (μm)	Sampling protocols	Air sheds	Mass and chemical anal.	Source Info	Meteorology
Washington, D. C., Aerosol Study Aug–Sep 1976[22]	Elem. compos. of particulate matter	Impactors, Nuclepore filters	Daily 24h samples for 6 weeks	Washington DC; Urban and Suburban	40 trace elem.; SO_4^-, NO_3^-, NH_4^+	Major sources	Local
NASN—Cascade Impactors 1970[23]	Size distribution of urban aerosols	Impactors (5 stage Andersen)	24h samples every second week	Chicago, IL; Cincinnati, OH; Denver, CO; Phila, PA; St. Louis, MO; Washington, DC	Mass	none	none
CHAMP 1971–1976[24]	For Community Air Pollution Health Studies	Various size ranges for cyclones, impactors, and modified Hi vols	24 h samples	Various U.S. cities including: Los Angeles, CA; New York, NY; Cleveland, OH; Birmingham, AL; Akron, OH; Salt Lake City, UT	Mass	none	none
Houston Aerosol Characterization Study Aug 5 to Oct 1 1976[25]	Chemical and Physical properties of aerosols and assoc. with visibility	0–2.5 >2.5–15	12 h samples (Aug 5–Sep 1); 12h samples only between 6 am–6 pm (Sep 25–Oct 1)	Houston, TX	Trace elem., Mass, ions	none	none
Global Aerosol Measurements 1960s and 1970s[26]	Characterization of aerosols in lower troposphere	Number concentration .005–10 for the various intervals	Periodic	Hundreds of urban, rural, continental and oceanic locations	Number concentrations	none	none
Inhalable Particulate Network June 1979 to present[27]	Particle size in cities having had health studies; control strategies	0–2.5; 0–15; >2.5–15; 0–30 BS (at some sites)	24h samples; every 6th day; every 3rd Phil (3 sites); each day (Phil)	40 urban centers in US	Mass (all) trace elem; SO_4^-, NO_3^- (every 4th samples)	none	NWS
Denver Brown Cloud Study Nov–Dec 1978[31]	Characterization of Denver air Pollution and haze	Continuous size dist. 0.01–10, Fine particle mass >2.5 (4h, 24h)	Daily	Seven sites in and around Denver	Mass, SO_4^-, NO_3^-, C, NH_4^+, trace elements	Emission inventory	Local and synoptic

APPENDIX B

DATA SUMMARY FORMS

TABLE B-1. CHEMICAL CHARACTERIZATION

Element	Source associated with this element	Concentration µg/m^3			
		Mean	High	Low	St. Dev.

TABLE B-2. SIZE DISTRIBUTION SUMMARY

Study	<1 μm		<2.5 μm		<10 μm		<15 μm		2.5-15 μm		Measured by hi-vol. <30 μm	
	$\mu g/m^3$	% total mass	$\mu g/m^3$	% total mass	$\mu g/m^3$	% total mass	$\mu g/m^3$	% total mass	$\mu g/m^3$	% total mass	$\mu g/m^3$	% total mass